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Synthesis and characterization of a polysulfone based polymer inclusion membrane

Kunene, Phumlile Promise

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SYNTHESIS AND CHARACTERIZATION OF A POLYSULFONE BASED POLYMER INCLUSION MEMBRANE



Phumlile Promise Kunene

A dissertation submitted to the Faculty of Science, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Master of Science

University of the Witwatersrand

Johannesburg

December 2018

DECLARATION

I declare that dissertation is my own unaided work. It is being submitted for the Degree of Master of Science to the University of the Witwatersrand, Johannesburg, South Africa. It has not been submitted before for any degree or examination to any other University.

……

Miss Phumlile Promise Kunene

School of Chemistry, University of the Witwatersrand, Johannesburg

ABSTRACT

Poly(vinyl chloride) and cellulose triacetate are the most extensively used and studied base polymers for preparation of polymer inclusion membranes used in water purification. However, their instability under extreme conditions has brought about the need to explore other base polymers that can overcome such limitations. In this study we investigated polysulfone as an alternative base-polymer that could possibly withstand harsh environmental conditions and have good transport efficiency towards metal ions. Polymer inclusion membranes were prepared using polysulfone as a base polymer and Aliquat 336 as a carrier. Chromate was used to study the extraction efficiency of the membranes. The optimal composition ratio for the membrane that gave the highest extraction efficiency of chromate from solution was 40:60 %w/w polysulfone: Aliquat 336, with a flux of $8.68 \times 10^{-7}\ mol\, m^{-2} s^{-1}$. The polysulfone based membrane prepared during this study was found to have increased chemical stability over a range of pH 2 – 12 compared to poly(vinyl chloride) based membranes.

The presence of functional groups on the polysulfone, Aliquat 336 and the synthesized polymer inclusion membrane were confirmed using Fourier Transformed Infrared Spectroscopy. The results revealed that only physical interaction exists between the carrier and the polymer matrix. Scanning electron microscopy and atomic force microscopy were used to characterize the surface morphology. The membranes were found to be dense and their roughness increased with an increase in carrier concentration. The hydrophilicity of the membranes was studied using a drop shape analyser. The results revealed that an increase in carrier concentration increases the membranes' hydrophilicity. Thermal stability was investigated using a thermogravimetric analyser and the membranes were found to be stable up to 180 ºC.

DEDICATION

This dissertation is dedicated to the following:

My Brother Alex Muzi Kunene. Thank you Ntimandze Lobhambo for believing in me when I did not believe in myself. Your immeasurable support and motivation has made me the woman I am today. Ngiyabonga Madvonsela, Kunene, Mntimandze, Lobhambolunye, tingaba timbili tetanamake kaMabuza. I am forever grateful Vusamuti.

My friend Dudu Thabile Nkuna. Thank you for being more than just a friend. I will forever be grateful for your love and support through the good, the bad and the tragic. I would have not made it this far without you.

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ABBREVIATIONS

2-NPOE	2-nitrophenyl octyl ether
2-NPPE	2-nitrophenyl pentyl ether
CAB	Cellulose acetate butyrate
CAP	Cellulose acetate propionate
Cr	Chromium
CTA	Cellulose triacetate
CTB	Cellulose tributyrate
DGT	diffusion gradient in thin-films
DMAc	Dimethylacetamide
ILM	immobilized liquid membranes
ISE	Ion selective electrode
LDPE	low-density polyethylene
LM	Liquid membrane
MESCO	Membrane Enclosed Sorptive Sampler
PIM	Polymer inclusion membrane
PLM	Permeation liquid membrane
POCIS	Polar Organic Compound Integrative Sampler
PVC	Poly (vinyl chloride)
PVDF	Poly(vinylidene fluoride)
PVDF-HFP	Poly (vinylidene fluoride-co-hexafluoropropylene)
SPMD	Semi-permeable membrane device
USGS	United States geological survey
WWTPs	Wastewater treatment plants

Chapter 1

This chapter contains the background and motivation to this study.

1 Introduction

Water is an essential yet finite resource which plays a vital role in everyday sustainability of life on earth. Globally, the fresh water supply has been decreasing whilst its demand has tripled since the 1950s (Hanjra and Qureshi, 2010). There is a growing concern on the scarcity of water especially in the dry zones where there is heavy exploitation of the little water resources present (Elgallal, Fletcher and Evans, 2016). About 500 million people reside in water-scarce countries, and due to the drastic increase in the human population, it is estimated that the number will increase to about three billion by the year 2025 (Hanjra and Qureshi, 2010). With the water crisis increasing daily, the sustainability of human livelihood and the economic development is threatened especially, in the developing countries (Elgallal, Fletcher and Evans, 2016). The need for access to potable water will only grow more severe due to the depletion of natural freshwater sources. Without a resupply of the consumed freshwater the severity of water scarcity will eventually lead to increase in the risk of water based conflicts within communities.

Generally, the water demand has increased due to the growth in human population and the competition between agriculture and industry for water. Because of this, new sources of water had to be exploited. In many countries especially the water-stressed ones, recycling of wastewater has been recognised as a cheap, suitable and reliable source of water for various purposes including irrigation (Qadir, 2010; Elgallal, Fletcher and Evans, 2016). Wastewater has many benefits, which include providing nutrients for crops, reliability and low cost relative to conventional water sources. However, there are a number of drawbacks associated with it. Wastewater poses a risk to the environmental and human health primarily due to its association with microbial organisms and other toxic compounds like trace metals (Qadir, 2010; Elgallal, Fletcher and Evans, 2016). Release of trace metals into the environment is mainly due to anthropogenic activities especially mining activities while natural disasters such as forest fires, volcanic eruptions also contribute to these metals in water sources (Facchinelli, Sacchi and Mallen, 2001; Ebenebe, Shale and Sedibe, 2017). While some of these metals are essential for biological activities in both the human body and plants, they become toxic if consumed in

excess and result in a number of health effects (Facchinelli, Sacchi and Mallen, 2001).

Constant monitoring of pollutants in the wastewater treatment plants (WWTPs) water and other water bodies for detection of its point sources and to minimize or eliminate their emissions is vital. There has been great advancements in the development of analytical techniques and methods for analysing trace metals in different environments. However, there is still a number of challenges in both sampling and analysis. The challenges include the difficulty in determining pollutants in different complex matrices such as sediments. Most of these analytical methods require several steps which are time consuming and expensive processes (Chimuka, Cukrowska and Jönsson, 2004; Almeida et al., 2016). The most commonly used monitoring method involves spot sampling and since over time chemical concentrations varies, some of the pollution events are likely to not be accounted for (Almeida et al., 2016).To minimize cases of missed pollution events sampling is done more frequently, of which tends to be expensive and time consuming. Passive sampling methods like permeation liquid membrane (PLM) were developed to help address these issues (Vrana et al., 2005).

PLM is a form of passive sampling that uses the liquid-liquid extraction principles with the advantage of lesser toxic solvents and increased selectivity due to its incorporation of liquid membranes such as polymer inclusion membranes (PIMs) and supported liquid membranes (SLMs) (Parthasarathy, Pelletier and Buffle, 2004; Bayen et al., 2006). The effectiveness of this method is dependent on the stability of the membrane. PIMs are the most stable form of liquid membranes. They normally consists of a base polymer, carrier, and plasticizer. The base polymer holds the carrier and provides the membrane with mechanical strength (Nghiem et al., 2006; O'Bryan et al., 2016). The carrier acts as an ion exchanger or a complexing agent which binds with the target analyte and transports it across the PIM into a receiver solution(Almeida, Cattrall and Kolev, 2012; Bonggotgetsakul, Cattrall and Kolev, 2016). The plasticizer softens the membrane, hence increasing its flexibility by decreasing its glass transition temperature (Almeida, Cattrall and Kolev, 2012). Poly(vinyl chloride)(PVC) and cellulose triacetate (CTA) are the most commonly used base polymers (O'Bryan et al., 2016). However, they have

been found to be unstable under extreme conditions with PVC undergoing dehydrochlorination in alkaline medium (Shindo and Hirai, 1972; Kise, 1982; Yoshioka *et al.*, 2008b) whilst CTA which undergoes hydrolysis in highly acidic and basic medium (Gardner, Walker and Lamb, 2004; Puls, Wilson and Hölter, 2011; Casadella et al., 2016). This has brought about the need to explore other base polymers that can overcome such limitations enabling the use of this technology in broader environmental conditions.

In this study, we explored an alternative base-polymer that could overcome these limitations, whilst maintaining good or improved transport efficiency. We investigated polysulfone as a potential base polymer. Polysulfone is famous for its hydrophobicity, toughness and stability at high temperatures. It has good chemical and mechanical strength, it maintains its properties over a wide range of pH and has exceptional oxidative resistance (Majewska-Nowak, 1989; Huang and Yang, 2006; Richards, Baker and Iwuoha, 2012). As such, polysulfone is widely used in various industries for different applications like ultrafiltration membrane material for water treatment, biomedical applications and other industrial fields (Kim et al., 2002; Zhang et al., 2008, 2009; Ding et al., 2016)

Chapter 2

This chapter presents a brief overview of the literature relating to the development of polymer inclusion membranes

2 Literature review

2.1 Passive sampling

Passive samplers have been described as “any sampling technique based on free flow of analyte molecules from the sampled medium to a collecting medium, as a result of a difference in chemical potential of the analyte between the two media” (Seethapathy, Górecki and Li, 2008). Initially passive samplers were made for sampling in the air. In the early 1980s Aylott and Byrne developed the first passive sampler to be applied in aquatic environments, and recently they have been modified for solid matrices as well (Seethapathy, Górecki and Li, 2008).

Passive samplers are gaining popularity for assessing integrated, or time-weighted, concentrations of organic chemicals in aquatic systems (Vrana and Schüürmann, 2002). Unlike most of the monitoring methods passive samplers are relatively cheap and easy to use. Various types of passive samplers were developed over the last three decades (Vrana et al., 2005).

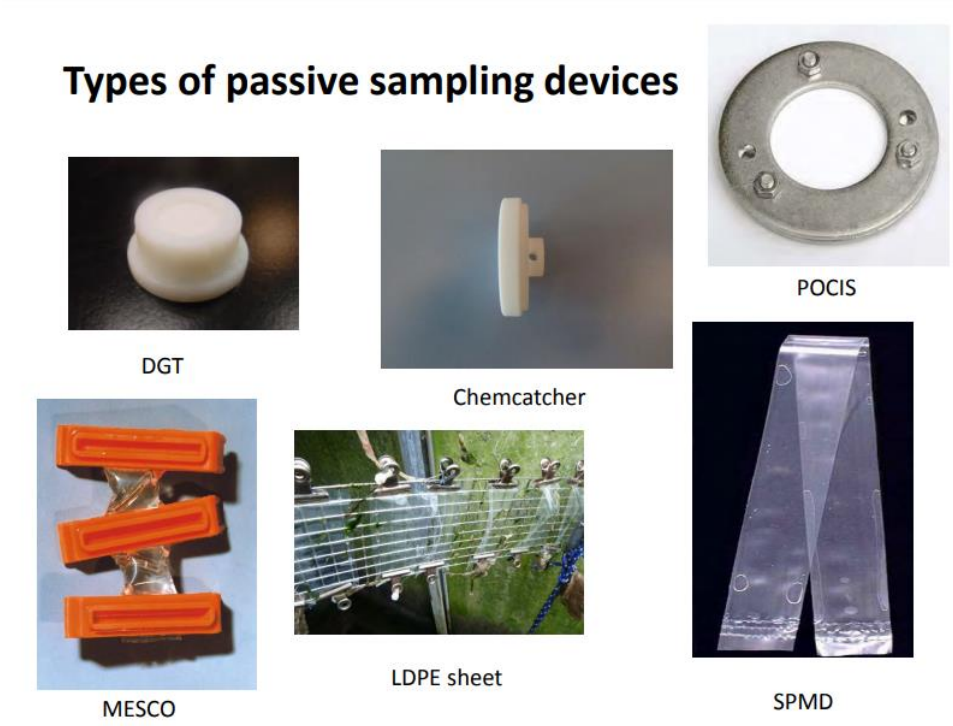


Figure 2.1 Different types of passive samplers (Mills and Gravell, 2015)

Figure 2.1 demonstrates some of the common types passive sampling devices. These include the semi-permeable membrane devices (SPMDs), diffusion gradient in thin-films (DGT), membrane enclosed sorptive sampler (MESCO), polar organic compound integrative sampler (POCIS), chemcatcher, and low-density polyethylene (LDPE) (Almeida *et al.*, 2014).

The passive samplers are utilized in various environments and environmental conditions, depending on the specific design of each. DGT was reported as the most commonly used when monitoring metal ions (Almeida *et al.*, 2014). Prest *et al.*, (1995) investigated the application SPMDs in sampling of trace organic contaminants in water and air. It was concluded that the SPMD has a bright future in the field because of its ability to mimic aquatic organisms' properties like their bioconcentration mechanisms providing insights on the bioaccumulation processes.

The usual makeup of passive samplers involves the separation of the receiving phase from the source phase by a semipermeable membrane (Vrana *et al.*, 2005). The type of membrane used depends on the target analyte and dictates at what rate the analytes will be collected into the receiving phase (Almeida *et al.*, 2014).

2.2 Liquid membranes

Membranes have been described by the International Union of Pure and Applied Chemistry as heterogeneous phases that prohibit the flux of chemical species in liquid or vapour phase (Ramkumar and Chandramouleeswaran, 2015). Separation occurs when one component of the mixture travels through the membrane faster than the other (Kislik, 2010; Ramkumar and Chandramouleeswaran, 2015). Membranes can either be in the form of solid or liquid state. Liquid membranes (LMs) have a larger flux compared to the solid membranes because liquids have diffusion coefficients higher than those of solids (Kislik, 2010). This means that in LMs the separation occurs relatively faster.

Liquid membrane (LM) systems have become an attractive alternative separation method due to their relatively environmentally friendly properties compared to conventional methods (Kagaya *et al.*, 2012; Cho, Cattrall and Kolev, 2018). A LM scheme consists of a liquid that serves as a semipermeable barrier. The liquid is

insoluble in both the source and the receiving solutions (Kislik, 2010). Liquid membranes systems mimic the properties associated with those of traditional separation techniques such as liquid-liquid extraction without the consumption of large quantities of flammable, toxic and volatile organic solvents. As a result there has been a lot of interest in their use for separation in chemical analysis and industrial processes (Bonggotgetsakul *et al.*, 2010; Kagaya *et al.*, 2012).

LMs can be classified into supported and non-supported liquid membranes depending on whether polymeric support is present or not in the liquid phases (de Josefina and de Eduardo Rodriguez., 1999). The common types of LMs are supported liquid membrane (SLM), emulsion liquid membrane (ELM), and bulk liquid membrane (BLM) (de Josefina and de Eduardo Rodriguez., 1999).

2.2.1 Bulk liquid membranes (BLM)

Bulk liquid membrane (BLM) is a form of liquid membrane where a water-immiscible liquid phase (usually an organic solvent) serves as a barrier between the aqueous feed and receiver solution. When the feed and receiver solutions are water-immiscible an aqueous membrane is employed as a barrier between them. It is the most popular type of LM (Kislik, 2010; Diaconu *et al.*, 2016). Microporous support materials may sometimes be used to separate the liquid membrane from the feed and receiver phases. These materials form the bases of the different terms sometimes used when referring to BLMs. The terms include hollow-fibre, flat neutral, ion-exchange sheet, etc. (Kislik, 2010). BLMs have the simplest experimental systems designs for executing a LM process and it also demonstrates great stability (Nabieyan *et al.*, 2007; Chang, 2016). They can then be classified based on the design of the experimental system and the density differences between the membrane and the feed and receiving phases. The types of BLM systems include, wall in wall, H-type, U-type, etc. (Diaconu *et al.*, 2016). Examples of the different systems are demonstrated in Figure 2.2.

BLMs attract a lot of researcher's attention because of their simplicity and stability. However, they have low transport efficiency. This is attributed to the low interfacial surface areas and the thickness of the membrane resulting in long pathways that analyte has to travel (Nghiem *et al.*, 2006; Chang, 2016; Bartsch and Douglas Way,

2018). Consequently, though BLMs are good for laboratory scale work they are impractical for industrial and field work.

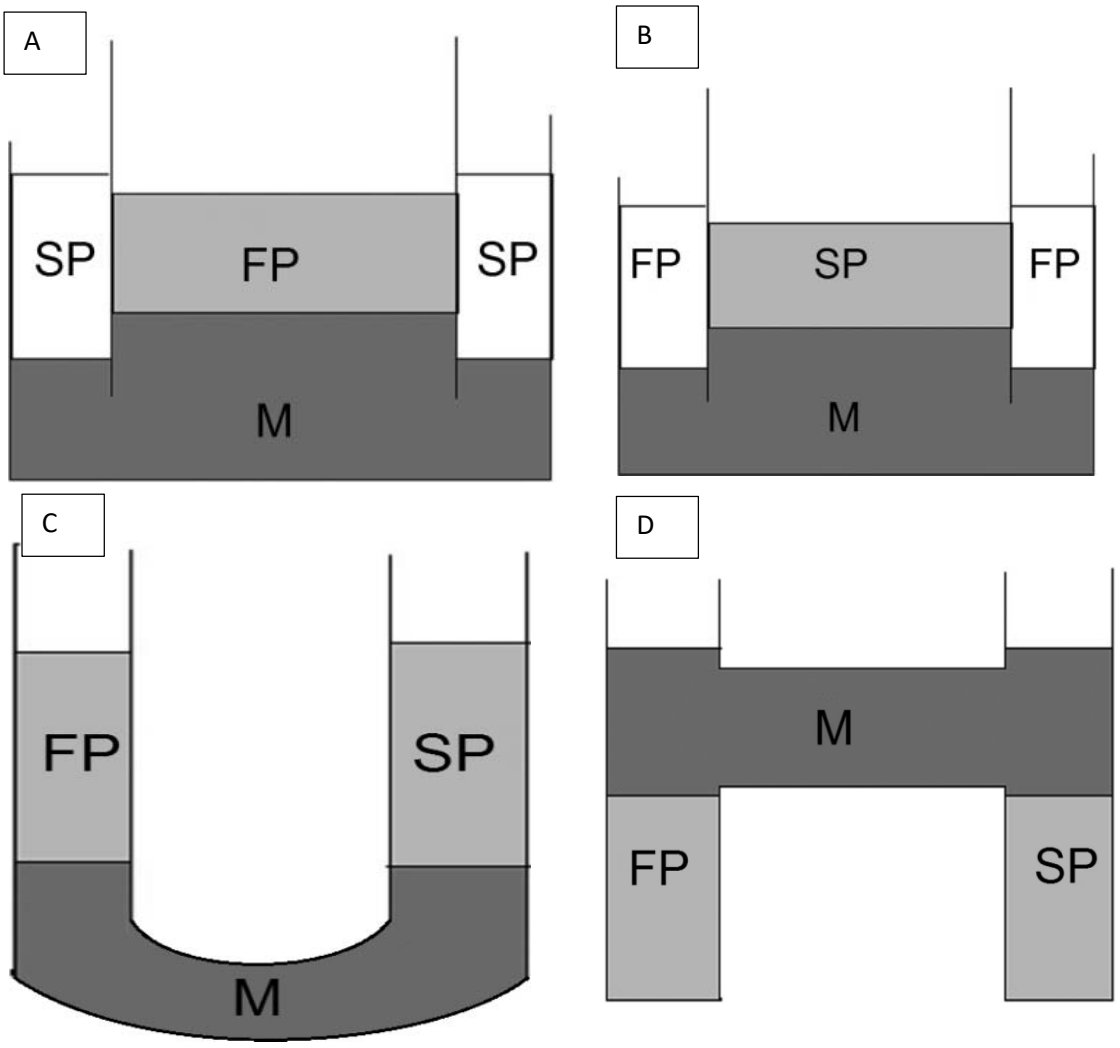


Figure 2.2 Different BLM systems Experimental devices for BLM: (A) and (B) wall in wall, (C) U-type, and (D) H-type (FP-feed phase, SP-stripping phase or receiving phase, M-membrane) (Diaconu *et al.*, 2016).

2.2.2 Emulsion liquid membranes (ELM)

Emulsion liquid membrane was invented by Li for hydrocarbons separation in 1968 (Raghuraman, Tirmizi and Wiencek, 1994; Chakraborty, Bhattacharya and Datta,

2010; Kislik, 2010; Ahmad *et al.*, 2011; Bartsch and Douglas Way, 2018). Since then it has been extensively studied and utilized for separation of different organic and inorganic compounds, even at trace levels. ELMs are also referred to as double emulsion systems because they facilitate transport and whilst simultaneously separating the feed and stripping phases. They can be classified into two types' oil-in-water and water-in-oil with water-in-oil being the most commonly reported in literature (Chakraborty, Bhattacharya and Datta, 2010; Kislik, 2010). When feed is an aqueous solution the water-in-oil system is used where the immiscible oil phase is the membrane phase separating the aqueous feed and stripping phases; and when dealing with an organic feed solution the oil-in-water system is used where the aqueous solution is the membrane phase responsible for keeping the two organic phases (feed and stripping) from mixing (Raghuraman, Tirmizi and Wiencek, 1994; Chakraborty, Bhattacharya and Datta, 2010).

A primary water-in-oil ELM is made out of two immiscible phases, the stripping solution and the organic liquid membrane phase which may at times contain a carrier which facilitates the extraction process, emulsified with a surfactant to produce an emulsion (Kislik, 2010; Othman, 2016). This is then dispersed into the feed/contaminated solution to be treated by mechanical agitation. The mass transfer of analytes occurs through liquid membrane phase between the feed and internal (stripping) phase (Othman, 2016). To elute the analytes demulsification has to occur. Using high voltage electric fields has been proven to be the best method (Raghuraman, Tirmizi and Wiencek, 1994). When eluting trace metals (inorganics) from the receiver phase, electroplating and/or crystallization are often used and the receiver phase can be recycled (Raghuraman, Tirmizi and Wiencek, 1994).

The advantages this separation process possesses include its ability to have extraction and stripping processes concurrently occurring in a single step which eliminates the equilibrium limitations experienced by traditional methods; the significant reduction of toxic and expensive solvent amounts compared to traditional methods; increased transport efficiencies (high flux); and high selectivity (Raghuraman, Tirmizi and Wiencek, 1994; Othman, 2016). For the ELM to be effective the emulsion needs to be able to withstand the shear force caused by the mechanical agitation whilst at the same time be easily broken to enable recovery of

the receiver phase (Kislik, 2010; Bartsch and Douglas Way, 2018). These two parameters need to be balanced and their contradictory nature results in stability being a major drawback for the ELMs.

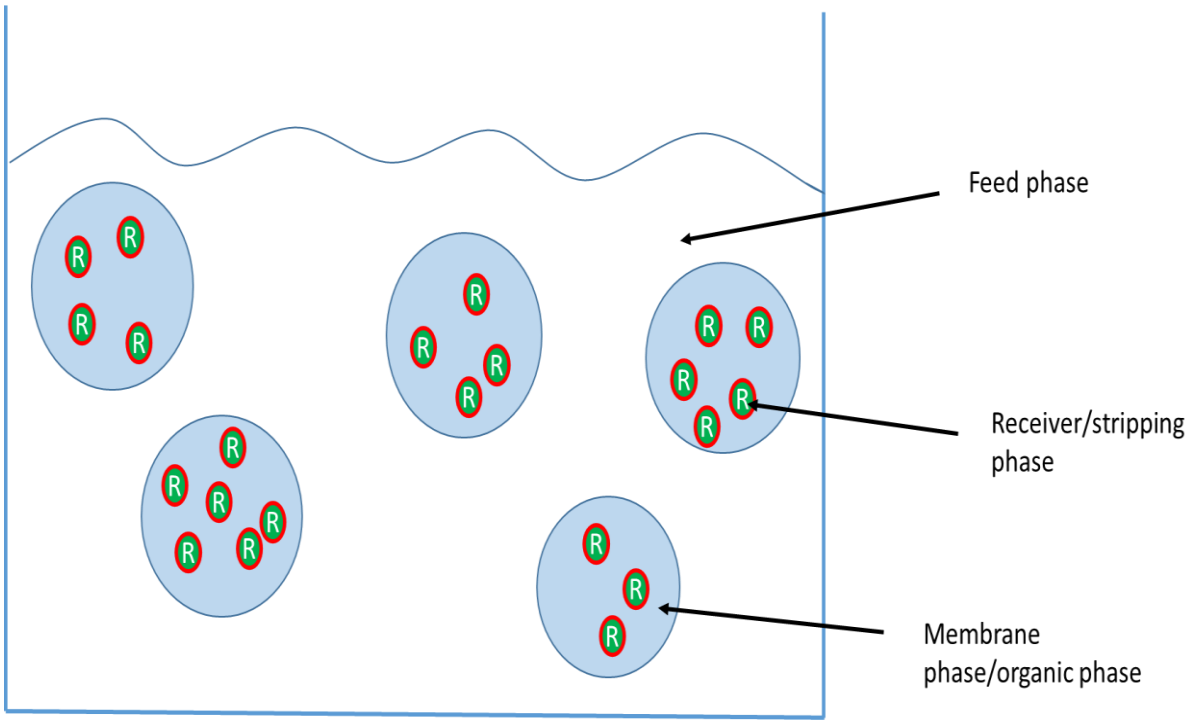


Figure 2.3 Emulsion liquid membrane (EML) extraction cell setup

2.2.3 Supported liquid membranes

Supported liquid membranes (SLM), also referred to as immobilized liquid membranes (ILM) are one of the most important form of liquid membranes. They are composed of an organic solvent and inert microporous support material. An organic solvent gets impregnated in the pores of a suitable inert microporous support material, creating a barrier between the aqueous feed and receiving/stripping phase (Chimuka, Cukrowska and Jönsson, 2004; Kislik, 2010; Parhi, 2012). The difference in concentrations between the feed phase and the receiving phase is utilized as a driving force for the transport of analytes through the organic membrane to the receiving phase by means of diffusion (Chimuka,

Cukrowska and Jönsson, 2004). For the maintenance of concentration gradient the analyte of interest must exist in both neutral and ionic state making the system/technique suitable only for ionisable compounds. In the donor phase the analyte should be at a neutral state to enable extraction by the membrane; it should then get ionized in the receiving solution to enable irreversible trapping (Chimuka, Cukrowska and Jönsson, 2004).

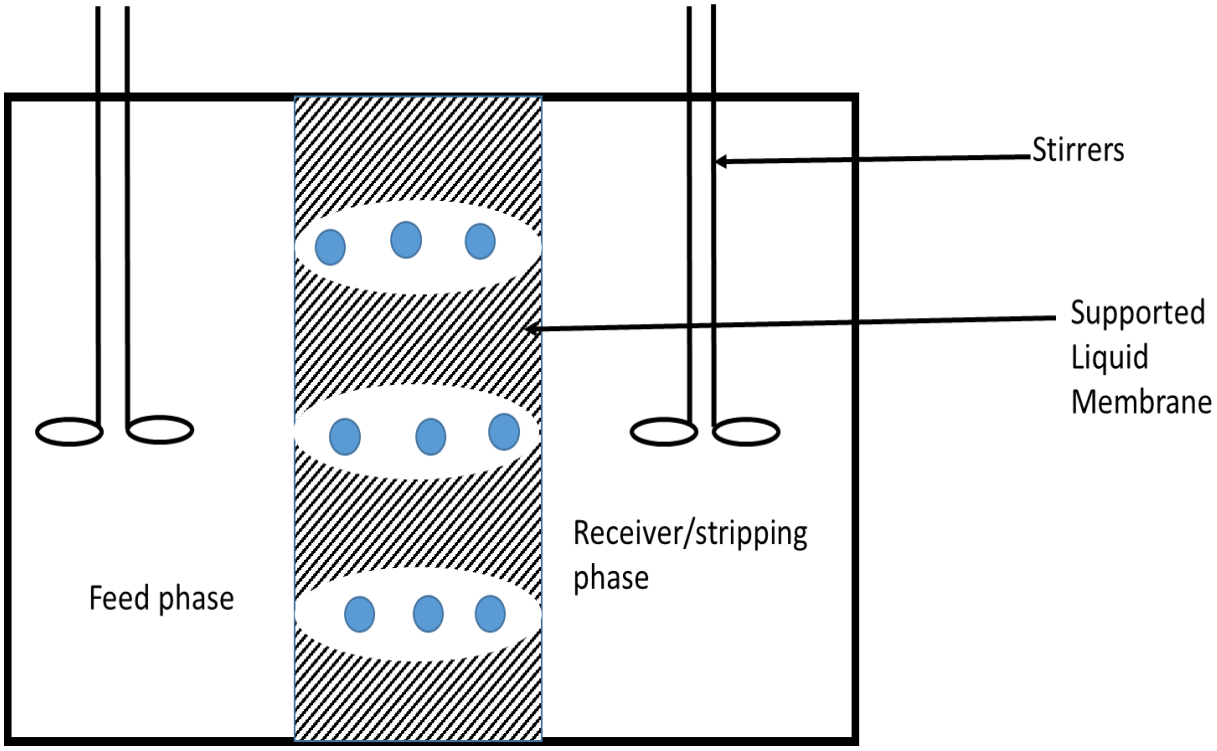


Figure 2.4 Supported liquid membrane (SLM) extraction cell setup

The SLM technology has been established as one of the best alternative method to conventional separation methods for extraction of a variety of compounds including, metals ions, organics and biological compounds (Malik, Hashim and Nabi, 2011). This is attributed to its highly selective whilst simultaneously enriching extraction technique (Muthuraman and Palanivelu, 2006). Advantages of this method include, low energy usage, simple to synthesize and operate, low operational cost, and relatively low organic solvents consumption (Malik, Hashim and Nabi, 2011). The usage of very little organic solvent during synthesis makes it possible to use expensive carriers which heightens the selectivity of the method

without it being too expensive (Kocherginsky, Yang and Seelam, 2007). Another advantage of the method is its ability to overcome equilibrium conditions, resulting in better mass transfer compared to conventional methods (Parhi, 2012).

SLMs have not been utilized much for industrial use. This is due to some concerns about the lack of long term stability of the membrane; the mechanical stability of the support material and the chemical stability of the organic solvent which reduces the membrane performance over time (Kislik, 2010; Malik, Hashim and Nabi, 2011) . Other issues concerning the SLM include the toxic effects of the volatile organic solvents (Malik, Hashim and Nabi, 2011).

2.2.4 Polymer inclusion membranes (PIM)

The concept of liquid membranes that are polymer-based has been researched for over 40 years and it has been identified as a potential replacement for the conventional solvent extraction (Almeida, Cattrall and Kolev, 2012). These polymer-based membranes are now called the polymer inclusion membranes (PIMs) and they have demonstrated good stability and versatility relative to other known liquid membranes like the SLM, BLM and ELM (Almeida, Cattrall and Kolev, 2012). Of the different types of liquid membranes PIMs are the most recent and they are gaining popularity due to their applicability in various fields and environmental conditions (Bonggotgetsakul *et al.*, 2010). Different PIM extraction cells are represented in Figure 2.5.

PIMs are a thin, stable and flexible form of liquid membranes (Gherasim *et al.*, 2011; Kagaya *et al.*, 2012) They are composed of a base polymer, a carrier also known as an extractant or ion-exchanger and a plasticizer (Vázquez *et al.*, 2014). PIMs have been successfully designed for the separation of different species such as metal ions, small molecules and inorganic anions (Vázquez *et al.*, 2014) and they are largely utilized as chemical sensors (Zawierucha, Kozlowski and Malina, 2016).

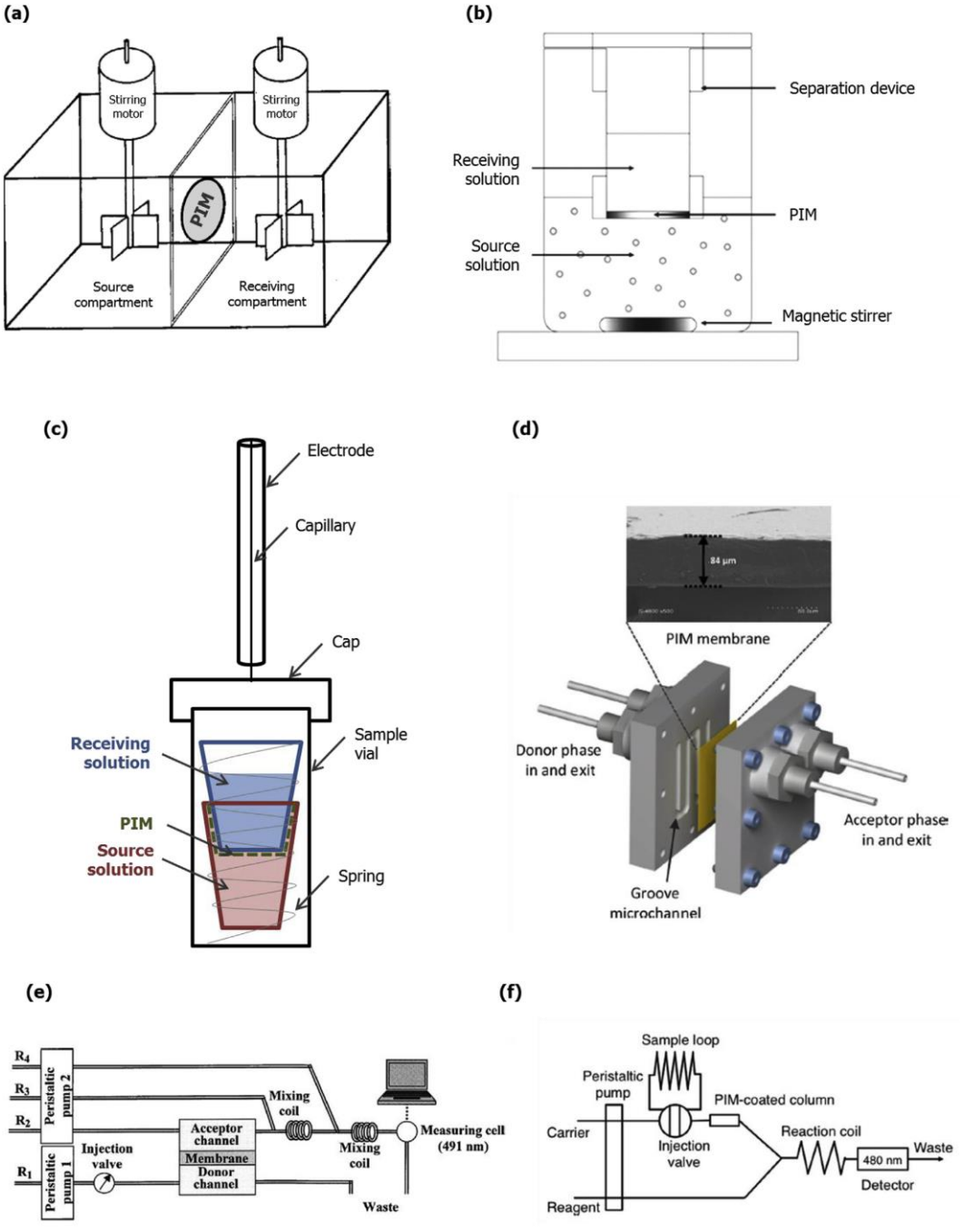


Figure 2.5 Variety of Schemes representing PIM-based extraction cells that have been utilized for separation and pre-concentration by means of passive diffusion based membrane transport. (a) Two compartment transport cell (b) Separation device (c) Microextraction device. (d) Micro-channel cell. (e) Flow injection analysis systems with on-line separation and detection utilizing a flat-sheet PIM. (f) PIM-coated column (Almeida, 2012)

A PIM is synthesized by dissolving a base polymer, carrier, and a plasticizer in an appropriate solvent which is then evaporated (Nghiem *et al.*, 2006; Gherasim *et al.*, 2011; Kagaya *et al.*, 2012). This process results in the immobilization of the carrier of choice in the plasticized polymer matrix forming a thin, stable and flexible membrane film. Each component of the membrane plays a vital role to ensuring its separation efficiency (Yildiz *et al.*, 2014). The base polymer holds the carrier and provides the membrane with mechanical strength (O'Bryan *et al.*, 2016). The carrier acts as an ion exchanger or a complexing agent which binds with the target analyte and transports it through the PIM (Almeida, Cattrall and Kolev, 2012). The plasticizer decreases the glass transition temperature of the membrane (Almeida, Cattrall and Kolev, 2012) and thus softening and increasing its flexibility (Vázquez *et al.*, 2014; Garcia-Rodríguez *et al.*, 2015). Some ionic liquids like Aliquat 336 at room temperature can act as both a carrier and a plasticizer, in such cases, it is not necessary to add a plasticizer (Gherasim et al., 2011; Almeida, Cattrall, and Kolev, 2012, 2017; Vázquez et al., 2014). Since plasticizers are expensive, using these ionic liquids is a cost-effective approach.

During synthesis the carrier is trapped by the plasticized base-polymer forming a gel-like network (Yildiz *et al.*, 2014; Salar-García *et al.*, 2015). This results into a flexible and stable self-supporting membrane that is applicable in the selective separation of target compounds in a similar process to that of the SLM (Nghiem *et al.*, 2006; Zawierucha, Kozlowski and Malina, 2016). However, greater stability and lifespan is achieved with the PIMs relative to its counterparts (i.e. SLM, BLM and ELM) due to the immobility of the non-polymer components (i.e. carrier) of the membrane within a polymer chain matrix (O'Bryan *et al.*, 2016).

Recently, due to their stability PIMs have attracted a lot of attention as an alternative to SLM (Garcia-Rodríguez *et al.*, 2015). It has been recognized that PIMs are highly stable because in comparison with the other liquid membranes only small amounts of the membrane liquid phase are lost to the aqueous phase it gets into contact with (Kagaya *et al.*, 2012). Other advantages associated with PIMs include their simple and easy preparation methods, good chemical resistance and mechanical properties that are better than those of SLM (Yildiz *et al.*, 2014; Salar-García *et al.*, 2015), and the use of significantly reduced amount of carrier which allows for the utilization

of more expensive materials without the membrane being too expensive (Zawierucha, Kozlowski and Malina, 2016). PIMs have significant resemblance to SLMs. They both contain a carrier. The difference is that in a SLM the carrier is held within a membrane polymeric structure whilst in a PIM it is incorporated into the base polymer and held together by capillary forces. This explains the great stability of the PIMs with respect to losing the extractant into the aqueous phase compared to SLMs (Bonggotgetsakul *et al.*, 2010).

Carriers

The extractant which is commonly referred to as a carrier acts as an ion exchanger or a complexing agent which binds with the target analyte and transports it through the PIM (Almeida, Cattrall and Kolev, 2012). The carrier which is stabilized by the base polymer in the membrane forms a complex or an ion-pair with the target analyte and then facilitates the transport of the analyte across the membrane from feed to receiver phase.

Carriers can be categorized or classified based on their physicochemical properties. The types of carriers include basic, acidic, macrocyclic, macromolecular and neutral\solvating. The most common types are basic, acidic and neutral\solvating carriers (see Figure 2.6) (Nghiem *et al.*, 2006; Zawierucha, Kozlowski and Malina, 2016). This types of carriers have been extensively investigated and applied in industry for hydrometallurgical applications (Cox, 2004). These carriers include the basic carriers such as the quaternary amines, tertiary amines, pyridine and their derivatives, some acidic and chelating carriers such as the alkyl phosphoric acids, hydroxyquinoline, hydroxyoximes, b-diketones, and carboxylic acids (Nghiem *et al.*, 2006; Almeida, Cattrall and Kolev, 2012; Zawierucha, Kozlowski and Malina, 2016). Macrocyclic and macromolecular have been found to have great selectivity due to their specific host-guest complex (Walkowiak, Ulewicz and Kozłowski, 2002). However, they are rarely used due to their environmental implications, lack of full understanding of their characteristics and they are quite expensive for large-scale applications.

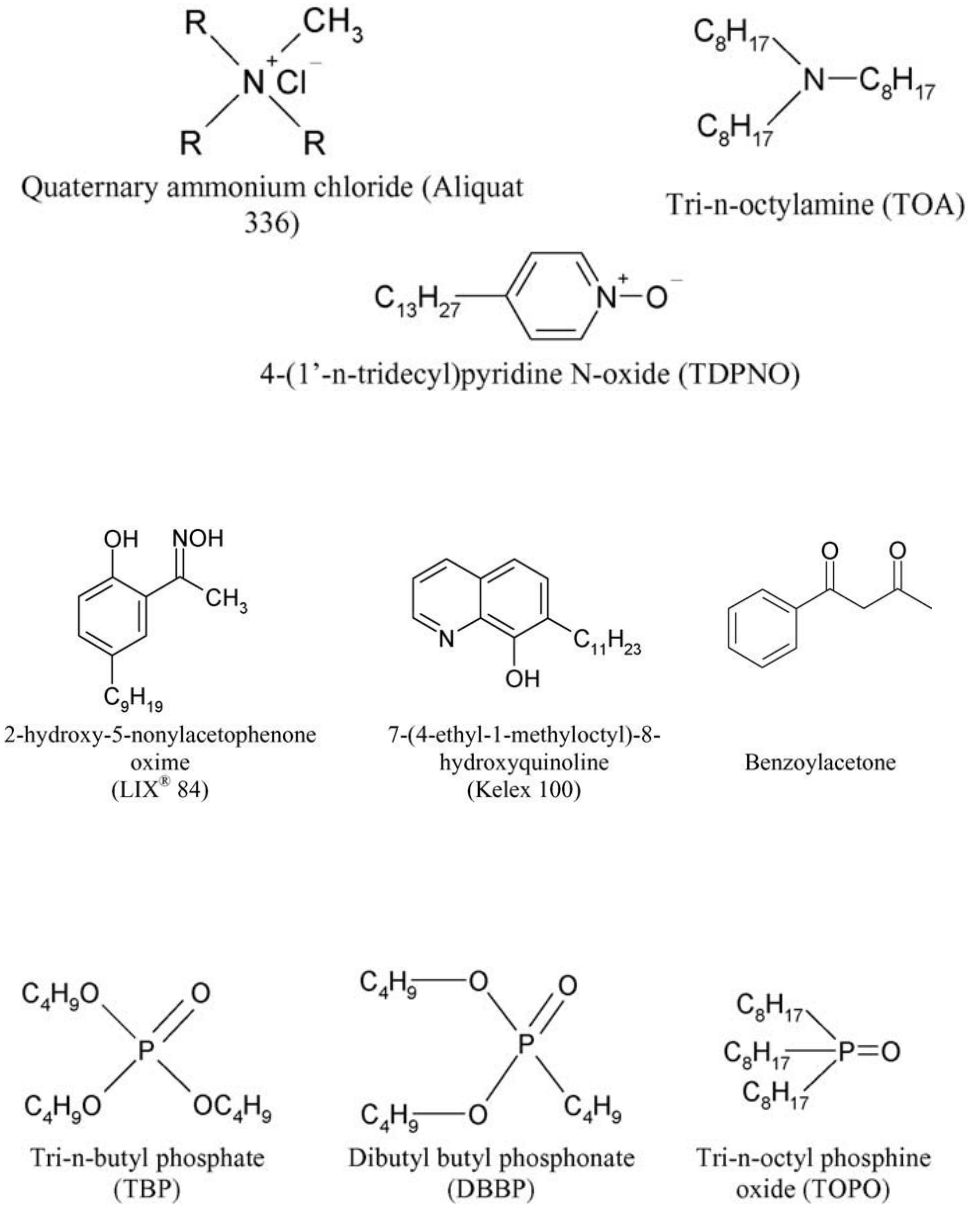


Figure 2.6 Chemical structures of the different types of carriers *(Nghiem* et al., *2006)*

A lot of research has been done on PIMs with different types of carriers, of which the focus has been mainly on the maximization of the membrane fluxes whilst simultaneously improving or retaining its selectivity and extraction efficiency. Various carriers will exhibit a variety of transport efficiencies, this is attributed to the different complexion mechanisms they each experience (Zawierucha, Kozlowski and Malina, 2016).

It is therefore vital to understand the physicochemical properties of the specific target analyte before choosing the type of carrier one will use. Aliquat 336 is a commercially available basic carrier which is amongst of the most commonly used and investigated(Almeida, Cattrall and Kolev, 2012). It has been successfully used for the extraction of thiocyanate, Cr(VI), Au(III), sulfonamides and tetracyclines, etc. (Bonggotgetsakul *et al.*, 2010; Cho *et al.*, 2011; Gherasim *et al.*, 2011; Garcia-Rodríguez *et al.*, 2015; Cho, Cattrall and Kolev, 2018). Another commonly used carriers is D2EHPA an acidic carrier which has been utilized a lot for the extraction of metallic cations like Pb(II), Ag(I), Hg(II), Cd(II), Zn(II), Ni(II), Fe(III), Cu(II) (Nghiem *et al.*, 2006; Gherasim *et al.*, 2011; Almeida, Cattrall and Kolev, 2012; Shahira *et al.*, 2018).

Plasticizer

Plasticizers are generally a group of organic compounds containing an alkyl backbone with highly solvating polar groups. They are applied to improve the characteristics of polymers such as their flexibility and mechanical stability (Mihali and Vaum, 2012). The backbone is responsible for controlling the compatibility of the membrane components whilst the polar groups interact with the polymer's polar sites. It is vital to strike a balance between the polar and non-polar groups in a plasticizer. Sugiura, (1992) investigated the role of the alkyl backbone and the polar groups and it was found that when you have 2 or 3 polar groups in a homologous series the optimal alkyl chains carbon atoms is 12. When increased further the compound becomes more hydrophobic and viscous resulting in the suppression of its polar properties. However, an increase in polar groups results in the opposite. A decrease in the viscosity is observed resulting in an increase in the hydrophilicity, of which a further increase would end up making the plasticizer unusable.

In a PIM the flexibility is highly dependent on the intermolecular forces of the polymeric chains. When you increase the strength of the intermolecular forces the membrane is subjected to more rigidity (Nghiem *et al.*, 2006). The plasticizer interacts with the intermolecular forces of the polymer by penetrating between the polymer molecules, neutralizing the polar groups of the polymer with its own polar groups and thus lengthening the distance between the polymer molecules (Nghiem

et al., 2006). This results in the reduction in strength of the intermolecular forces between the polymer matrixes. Consequently, the glass transition temperature of the polymer decreases, softening and increasing the flexibility of the membrane (Almeida, Cattrall and Kolev, 2012; Vázquez *et al.*, 2014; Garcia-Rodríguez *et al.*, 2015; Zawierucha, Kozlowski and Malina, 2016; Shahira *et al.*, 2018). The amount of plasticizer required to soften the membrane is highly dependent on the type of plasticizer used and the type of polymer (Shahira *et al.*, 2018).

The properties of a plasticizer play a vital role in choosing a compatible plasticizer for a membrane. The significant properties include its concentration, dielectric constant, and viscosity. An ideal plasticizer is said to be one that is insoluble in water, does not facilitate ion exchange and can stabilize the carrier in the polymer matrix (Carey, 2015). However, while it is insoluble in water, assists in stabilizing the carrier and functions as a softener, it does not prevent the loss of carrier and it usually facilitates the transport of interfering ions across the membrane (Carey, 2015). It was found that even though the effect of plasticizer in transport efficiencies is significantly low compared to those of the carrier, the plasticizer-carrier ratio, it has a significant effect on the sensitivity of an ion selective electrode (ISE) (Carey, 2015). Dinten *et al.*, (1991) revealed that the amount of plasticizer used during membrane synthesis has an effect on the selectivity and lifespan of ISE. It is therefore important to choose a plasticizer that is best suitable for that particular polymer.

There are a number of plasticizers that are commercially available. However, the most commonly used in PIMs are 2-nitrophenyl octyl ether (2-NPOE) and 2-nitrophenyl pentyl ether (2-NPPE) (Nghiem *et al.*, 2006; Almeida, Cattrall and Kolev, 2012). This is most probably due to their high dielectric constant and low viscosity physicochemical nature (Shahira *et al.*, 2018). It has been reported that at high dielectric constant the ion pair created between the carrier and analyte of interest separates more efficiently (Shahira *et al.*, 2018). As a result, the association-dissociation process between feed and receiver phase occurs faster. However, the issue of possible selectivity deterioration resulting from the incorporation of plasticizer in PIMs remains unresolved.

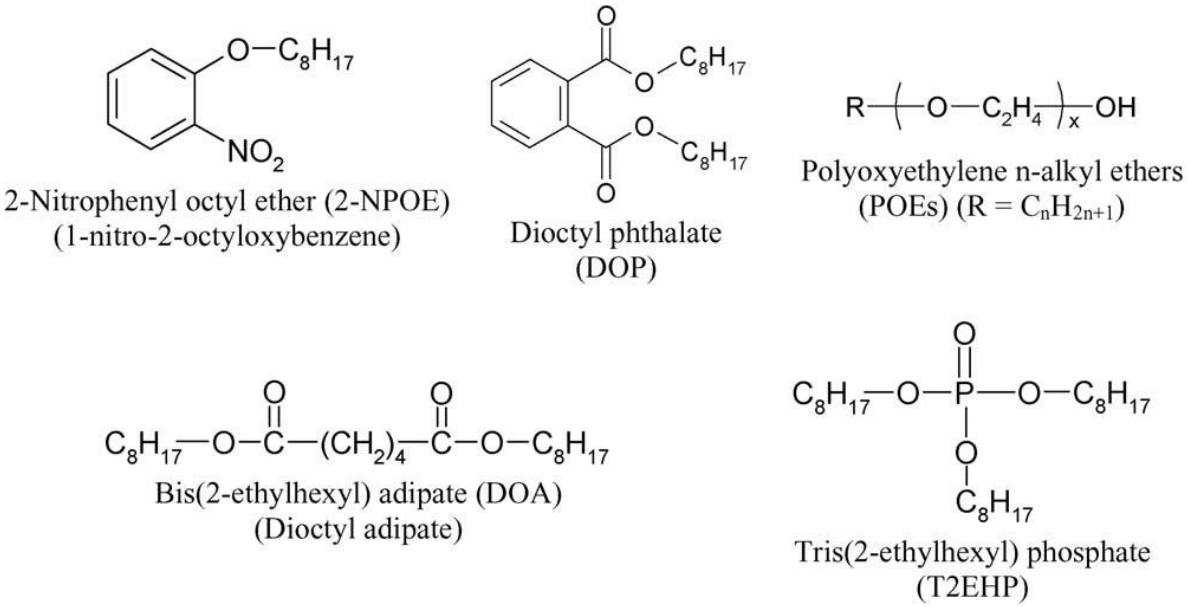


Figure 2.7 chemical structures of plasticizers commonly used in PIMs *(Nghiem* et al., *2006)*

Base polymers

The base-polymers normally used for the preparation of PIMs are thermoplastic polymers with weak physical bonds holding the polymer chains together (Gherasim *et al.*, 2011). Like the other components, they also play a crucial role in the PIM. Their core purpose is to ensure the entrapment of the carrier in their polymer matrix, making the membrane stable by minimizing the carrier loss to its surrounding solutions. They are also responsible for providing mechanical strength, whilst simultaneously causing minimal harm to the permeability rate of metal ions and small organic compounds in the membrane (Vázquez *et al.*, 2014; O'Bryan *et al.*, 2016; Zawierucha, Kozlowski and Malina, 2016). The polymer gets its mechanical strength from both the long chains entanglement and also its weak intermolecular forces (Wool, 1993). Highly stable membranes are formed when the molecular weight of the base-polymer used is greater than that of the critical entanglement molecular weight (Gherasim *et al.*, 2011).This is because below the critical entanglement molecular weight the polymer is unable to form strong entanglements it would therefore result in the carrier being easily lost to surrounding solutions.

The most commonly used base-polymers in the synthesis of PIMs are the poly (vinyl chloride) (PVC) and the cellulose triacetate (CTA) (Gherasim *et al.*, 2011; Yildiz *et al.*, 2014; O'Bryan *et al.*, 2016; Zawierucha, Kozlowski and Malina, 2016). This is due to their thermoplastic properties which enables them to easily dissolve in organic solvents (Shahira *et al.*, 2018). PVC based PIMs are known for exhibiting good mechanical strength and flexibility, they are also said to have high chemical resistance (Gherasim *et al.*, 2011). CTA has been widely used as a base polymer for PIM because it exhibits remarkable mechanical properties as a result of its highly crystalline structure, it is easy to work with and it is readily available (Gardner, Walker and Lamb, 2004). The CTA based membranes have been used in a variety of industries. Its applications include food packaging, films, moulding, surface coatings, lacquers, fibres, reverse osmosis materials, and filtration systems. CTA based PIMs have however been reported as less chemically resistant compared to the PVC based ones (Gherasim *et al.*, 2011).

Despite the evidence of good qualities PVC and CTA have as base-polymers for PIMs, they also have a number of drawbacks. When exposed to alkaline conditions PVC undergoes dehydrochlorination forming polyenes. As a consequence degradation of the membrane occurs, losing its mechanical stability. The degradation can be physically observed as it occurs with the membrane changing colour from a transparent thin film to a black one (Kise, 1982; Yoshioka *et al.*, 2008a). Under highly acidic and basic conditions the ester linkages in the cellulose backbone of the polymer are susceptible to hydrolysis resulting in the degradation of the membrane. (Gardner, Walker and Lamb, 2004). This is more likely under alkaline conditions, however, because CTA can be hydrated it becomes susceptible to hydrolysis even in acidic conditions (Zawierucha, Kozlowski and Malina, 2016). At room temperature if both polymers, PVC and CTA are without plasticizers their thin membranes are rigid. This is due to the high crystallinity of CTA and the high glass transition temperature (around 80°C) of PVC (O'Bryan *et al.*, 2016). The rigidity of the polymer matrix results in an increase in the diffusion resistance of the ion-pair mass transfer and thus lower extraction efficiencies. Even though plasticizers are used to make the membrane softer and more flexible, it is desirable

to use a polymer with low glass transition temperature. Such polymers are expected to allow for more efficient diffusion of the target analyte (O'Bryan *et al.*, 2016).

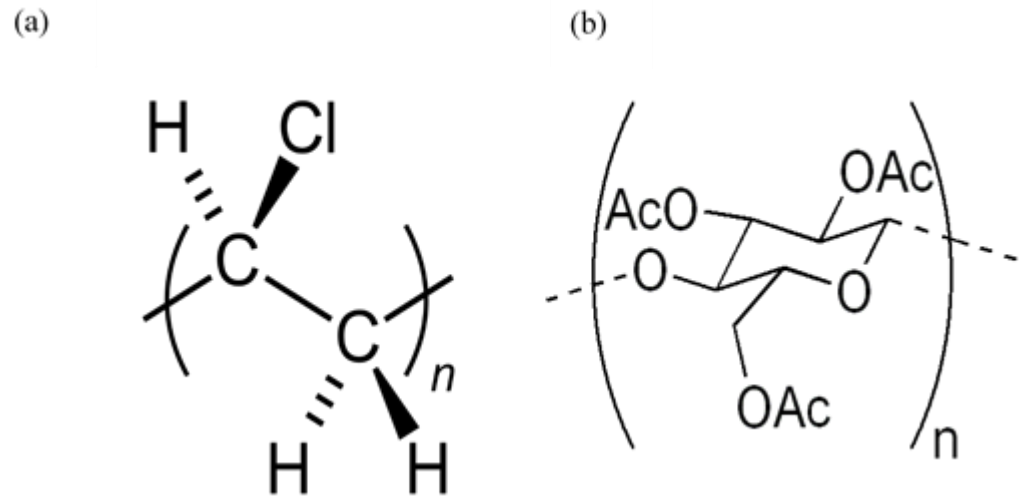


Figure 2.8 Chemical structures of (a) PVC and (b) CTA

In the last few years research has been done to explore other polymers as base-polymers for PIMs. A number of cellulose derivatives such as cellulose acetate propionate (CAP) and cellulose tributyrate (CTB) have been studied to determine their feasibility to be used as base polymers for PIMs (Rynkowska et al., 2018). Gardner et al. (2004), investigated cellulose derivatives cellulose acetate propionate (CAP), cellulose acetate butyrate (CAB) containing both high (B) and low (A) butyryl content, and cellulose tributyrate (CTB) as potential replacement for CTA in PIMs. The CAP, CAB and CTB based PIMs were successfully synthesized with bis-tert-butylcyclohexano-18-crown-6 as a carrier. Their properties were then compared to that of a CTA based PIM. The cation K(I) was used as a tool to investigate permeability of the membranes. Deterioration of flux was observed with an increase in size of the polymer side chain. Meaning CTA has better transport efficiencies that the other cellulose derivatives. However, the cellulose derivatives demonstrated remarkable durability with all of them maintaining stability for more than 65 days in acidic conditions whilst CTA hydrolysed in 12.25 days. In the basic conditions CTA hydrolysed at 2.9 days whilst CAB (B) was the most stable hydrolysing at 11.2 days. The derivatives showed good mechanical stability with

durability increasing with an increase in the polymer side chain. However, due to the decline in transport efficiencies they cannot utilized as replacement for CTA in PIMs (Gardner, Walker and Lamb, 2004).

Guo et al. (2011) investigated poly(vinylidene fluoride) (PVDF) as an alternative base polymer for PIMs for the extraction of Cr(VI), using different carriers. The membrane had an extraction efficiency of about 13 folds faster when using Cyphos IL 104 as carrier instead of Aliquat 336. This membrane demonstrated the ability to successfully extract the analyte of interest (Cr(VI)). However, when reusability (durability) studies were conducted, a decrease of about 69% in permeability was observed after 9 cycles, whilst only 33% decline was observed on CTA based PIMs over 6 cycles. This is attributed to the leaching out of carrier into the surrounding aqueous solutions, meaning the PVDF based PIMs lack stability compared to the CTA based PIMs (Guo et al., 2011).

O'Bryan (2016), investigated the use of poly(vinylidine fluoride-co-hexafluoropropylene) (PVDF-HFP) as an alternative base polymer. This polymer demonstrated great extraction efficiencies, with an initial flux of about 17 folds higher than that of the PVC based PIMs. This could be attributed to the low glass transition temperature the polymer possesses, which results in more flexible polymer chains and consequently a flexible membrane. The greater the flexibility of the polymer chains, the lower the ion-pair mass transfer diffusive resistance and thus better permeability rate. Membrane stability was also investigated by monitoring the mass loss after every extraction cycle using the same membrane. It was observed that the PVDF-HFP was significantly stable with a loss of only 4% of its original weight after 7 extraction cycles. However, the PVC based PIM was more stable losing less than 3% of its original weight on the 7th cycle. This brought about a concern on the durability of the PVDF-HFP based PIMs (O'Bryan *et al.*, 2016).

A comparison study was done by Wang et al. (2017) comparing the use of PVDF-HFP, PVC and CTA as the base-polymers for PIMs. LIX84I was utilized as the carrier of choice and 2-nitrophenyloctyl ether (NPOE) as plasticizer. Extraction studies were conducted with Cu(II) as an analyte of interest. The PVDF-HFP was

observed to have better extraction efficiency, reaching equilibrium after 1 h and complete extraction after 8 h. A yellow-green oily layer on the surface of the PVC and CTA based membranes was observed after extraction, whilst the PVDF-HFP based PIMs maintained a homogeneous surface. This was attributed to the loss of the organic phase to the aqueous phase. This resulted in low extraction efficiencies of the two membranes. The stability of the PVDF-HFP based PIMs was investigated and it was observed that about 10% of the original mass gets lost after 5 repeated cycles (Wang *et al.*, 2018).

In most of the alternative base polymers investigated stability remains the main issue. More research has to be done to find an alternative base polymer for PIM that will have good mechanical and chemical strength whilst maintaining good transport properties as well.

Polysulfone

In this study, we explored polysulfone as an alternative base-polymer that could possibly overcome the limitations of the common base polymers like PVC and CTA, whilst maintaining good or even improved transport efficiency. Polysulfone is a high-performance, tough, high-temperature-resistant thermoplastic polymer (Noshay and Robeson, 1976). Its structure contains benzene rings joined together by sulfonyl ($-SO_2-$), ether ($-O-$), and isopropylidene ($-C(CH_3)_2-$) groups.

Polysulfone is famous for its hydrophobicity, toughness and stability at high temperatures. It has good chemical and mechanical strength, it maintains its properties over a wide range of pH and has exceptional oxidative resistance (Majewska-Nowak, 1989; Huang and Yang, 2006; Richards, Baker and Iwuoha, 2012). As such, polysulfone is widely used in various industries for different applications like ultrafiltration membrane material for water treatment, biomedical applications, supporting layer for pervaporation membranes and other industrial fields (Kim *et al.*, 2002; Zhang *et al.*, 2008, 2009; Ding *et al.*, 2016).

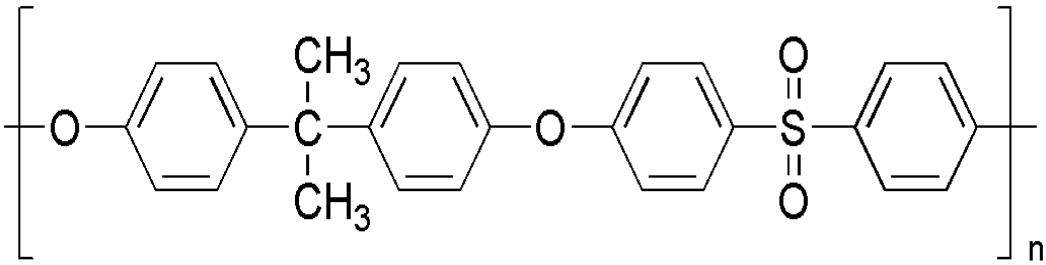


Figure 2.9 chemical structure of Polysulfone

Chapter 3

This chapter contains the aim and objectives of the study

3 Aim and objectives

3.1 Aim

The main aim of the research was to investigate the use of polysulfone as an alternative base polymer in polymer inclusion membranes (PIMs)

3.2 Objectives

This aim was achieved by addressing the following objectives:

- Optimization of polysulfone based polymer inclusion membrane synthesis methods by investigating the phase inversion and the solvent evaporation methods.
- Optimization of the PIM's composition ratio by doing the following:
    - Investigating mechanical stability of the membrane at different composition ratio
    - Investigating the effect of carrier composition on the membrane's transport efficiency
- Studying the chemical stability of the optimum membrane at different thicknesses in acidic and basic conditions
- Characterization of the polysulfone PIMs
- Doing a comparison study between the polysulfone based PIM properties and the properties to of a PVC based PIM

Chapter 4

This chapter contains a detailed summary of the preparation methods and materials and instruments used.

4 Materials and methods

4.1 Reagents

The following are the chemical reagents used for the accomplishment of this study.

Polysulfone pellets, poly(vinyl chloride),- tetrahydrofuran and Aliquat 336 were purchased from Sigma Aldrich (Johannesburg, South Africa). Chloroform and sodium hydroxide pellets were purchased from associated chemical enterprises (ACE) (Johannesburg, South Africa). Potassium chromate was purchased from May & Baker LTD (Dagenham, England).

4.2 Instrumentation

For casting membranes an Electrometer 3570 micrometric film applicator (Manchester, UK) was used. A Milli- Q-RO4 system (Millipore, Bedford, MA, USA) was used to purify deionised water. The pH of the solutions was measured using a Five easy FE20 pH metre purchased from Mettler Toledo (Johannesburg, South Africa). All metal ions were then analysed using an Agilent 7700 series ICP-MS (Kleve, Germany). Scanning electron microscopy (SEM) analysis was done to acquire information regarding membrane surface morphology. The images were recorded using a Carl Zeiss Sigma FESEM (Tokyo, Japan). Atomic force microscopy (AFM) analysis was carried out to investigate the roughness of the membrane surfaces. Images were obtained using a Veeco Di3100 AFM (Kleve, Germany). Fourier transformed infrared spectrometry (FTIR), IR spectra were recorded to determine the interactions between the polymer and the carrier in the PIM using a FT-IR Bruker Tensor 27 Spectrophotometer (Bruker, Germany) in transmission mode, of the range of 400 to 4000 cm^{-1}. Contact angle analysis was also done using a Kruss Drop Shape Analyzer, DSA30 (GmbH, Germany) to determine hydrophilicity of the PIM, and how the change in carrier concentration affects it. Thermal stability studies were carried out using TA Q600 SDT-Simultaneous Differential Scanning Calorimeter/Thermogravimetric analyser (Trossingen, Germany).

4.3 Membrane preparation method

4.3.1 Polysulfone based PIM synthesis

Phase inversion method

Polysulfone (PSF), Aliquat 336 and 2-Nitrophenyl octyl ether (2-NPOE) were mixed at various weight percentages. A mass of 2.00 g of the polysulfone, Aliquat 336 and 2-NPOE mixture was then dissolved in 25 mL of Dimethylacetamide (DMAc) by stirring for 3 h. The homogeneous solution was then casted in a glass plate using the automatic film applicator at thickness of 50 µm and slowly immersed in water. A white membrane sheet was obtained.

Solvent evaporation method

Polysulfone (PSF), Aliquat 336 and 2-Nitrophenyl octyl ether (2-NPOE) were mixed at various weight percentages. A mass of 1.00 g of the polysulfone, Aliquat 336 and 2-NPOE mixture was then dissolved in 10 mL of chloroform by stirring for 1 h. An automatic film applicator was then used to cast the solution on a glass plate at 50 µm thickness and it was left for 24 h to allow for complete evaporation of the solvent. The glass plate was then immersed in a water bath for the membrane to easily peel off. The membrane was then dried with paper towel.

4.3.2 Poly(vinyl chloride) (PVC) based PIM synthesis

A solution containing the fixed masses of PVC and Aliquat 336 at varying ratios were dissolved in tetrahydrofuran (THF) for 3 h. A mass/volume ratio of 1.00 g of PVC and Aliquat 336 mixture and 10 mL of THF was used. The resulting dissolved solution was then casted on a glass plate at 50 µm thickness using an automatic film applicator. The casted solution was then left to completely evaporate over 24 h. The glass plate was then immersed in a water bath for the membrane to easily peel off. The membrane was then dried with paper towel.

4.4 Extraction studies

Preliminary membrane transport studies were conducted in the laboratory using a passive sampling method. The experimental conditions were adopted from Gherasim *et al.*, (2011). A feed/donor phase solution of $500\ \mu g\ L^{-1}$ Cr(VI) at pH 4

in a beaker containing 200 mL deionised water was prepared. The membrane based passive samplers contained a 5 mL receiver solution chamber where 0.05 M NaOH receiver solution was added and it was sealed with a round cut PIM with an area of $3.14 \times 10^{-4}\ m^2$. The passive sampler was then deployed into the feed solution. The extraction study was done over a period of 3 h. The receiver solution was then analysed using an ICP-MS. The experiment was done in triplicates. This procedure was repeated for all membranes studied.

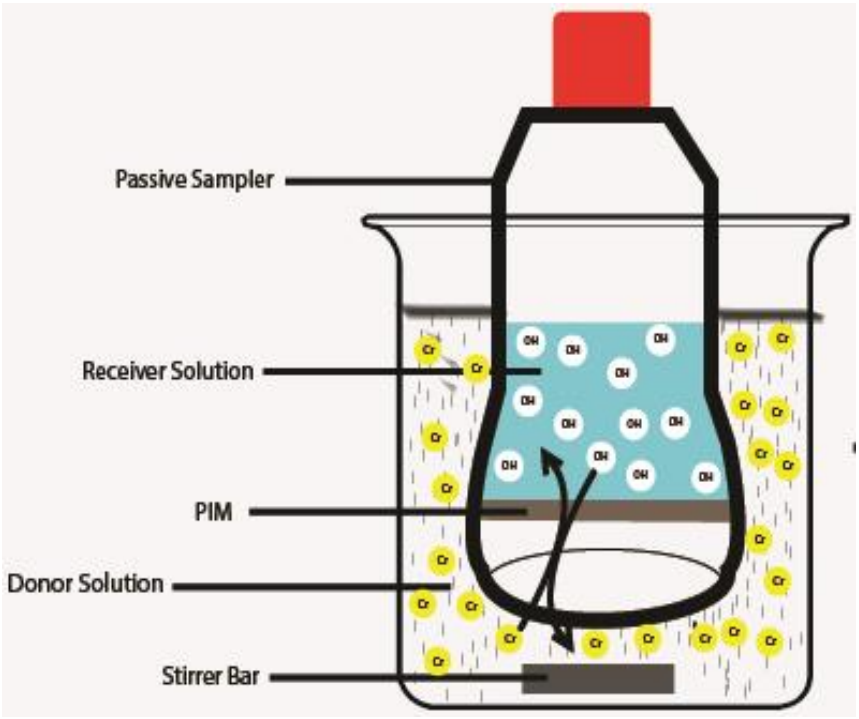


Figure 4.1 Sketch demonstrating the passive sampling setup

To measure the membrane's extraction efficiency the flux was then calculated with the formula (St John, Cattrall and Kolev, 2013):

$$J = \frac{V}{A} \times \frac{[Concentration]}{t} \qquad (1)$$

Where V is the Volume of feed, A= membrane surface area, [concentration] = concentration of the receiver solution, t = time of deployment, J = flux

4.5 Stability Studies

The chemical stability of both the PVC and PSF based PIMs was investigated in acidic and basic solutions using 1 M HNO_3 and 0.05 M NaOH respectively. The membranes were prepared and initial mass was taken. They were then placed in the acidic and basic solution and mechanically agitated for 24 h at 150 rpm. The membranes were then left to dry for another 24 h and reweighed. The average mass percentage lost was then calculated and reported.

Chapter 5

This chapter contains the detailed discussion of the results

5 Synthesis of PIM

5.1 Preparation method optimization

The physical structure and properties of a membrane are highly dependent on the material used and the method of preparation. The most common methods of membrane synthesis include phase inversion, sol–gel, films stretching, microfabrication vapour deposition and coating with phase inversion being one of the most important due to its morphology versatility and its simplicity (Ladewig and Al-Shaeli, 2017). Phase inversion technique can be used to synthesize different types of membrane by simply varying components like temperature of the water bath. In PIMs synthesis, solvent evaporation is the traditionally utilized method. This is a result of the dense membranes that it produces, enabling easy entrapment of the carrier and providing stability. However due to the toxic nature of the solvents used in the evaporation technique, an investigation was done to determine if phase inversion which is relatively a greener approach could produce mechanically stable PIMs.

PIMs of various composition containing PSF, Aliquat 336 and 2-NPOE (see Table 5.1) were synthesized using both solvent evaporation and the phase inversion method. Membranes were successfully synthesized using both methods. It was observed that for both techniques the control membranes (composed of 100% PSF) were mechanically stable, however they differed in colour. The one prepared by phase inversion was white whilst the one prepared via solvent evaporation was translucent. The rest of the PIMs both synthesized via phase inversion and solvent evaporation were white in colour. This could be due to the fact that when polysulfone gets in contact with water it changes from a transparent solution to a white solid. The colour change in the solvent evaporation prepared PIMs after addition of carrier and plasticizer could be a result of the PIMs becoming more hydrophilic as it was suggested by Vázquez et al., (2014) that the addition of Aliquat 336 results in an increase in hydrophilicity of a membrane surface. The newly found hydrophilicity of the membrane results in the absorption of moisture from air which then changes the colour of the membranes to white although it was not immersed in water.

Mechanical stability is one of the most significant properties of any membrane, as it determines its applicability. A membrane lacking mechanical stability is not viable for application as it will not be able to function properly under environmental conditions of interest. It is therefore vital that the PIM has good mechanical strength. The PIMs were considered mechanically stable when they could bend without tearing or visibly deforming. The solvent evaporation technique produced mostly stable membranes. When phase inversion technique was applied, the membranes produced were too soft with an oily surface suggesting that the membrane fails to trap the carrier into its polymeric matrix during the solidification process.

Table 5.1 Comparison of physical properties of PIMs synthesised via phase inversion and solvent evaporation

Composition (wt %)			Mechanical stability			
PSF	Aliquat 336	2-NPOE	Phase inversion		Solvent evaporation	
100	0	0	✓	Flexible	✓	Flexible
70	20	10	×	Soft	×	Stiff
60	20	20	×	Soft	×	Stiff
60	30	10	×	Soft	×	Stiff
50	30	20	×	Soft	✓	Flexible
50	20	30	×	Soft	✓	Flexible
40	40	20	×	soft	✓	Flexible

SEM analysis was conducted to determine the morphology of the PIMs prepared using both methods. For phase inversion prepared PIMs, when they were exposed to heat through the process of sample preparation, by coating the surface with carbon they started breaking. This is clearly shown in Figure 5.1. However the solvent evaporation prepared PIMs were stable during sample preparation and smooth dense surfaces were observed with minor surface defects (Figure 5.2). This is in agreement with the SEM results reported by Gherasim et al., (2011). Due to

the instability of the membranes when synthesized via the phase inversion, solvent evaporation was selected as the optimum method for the synthesis of the PSF based PIMs.

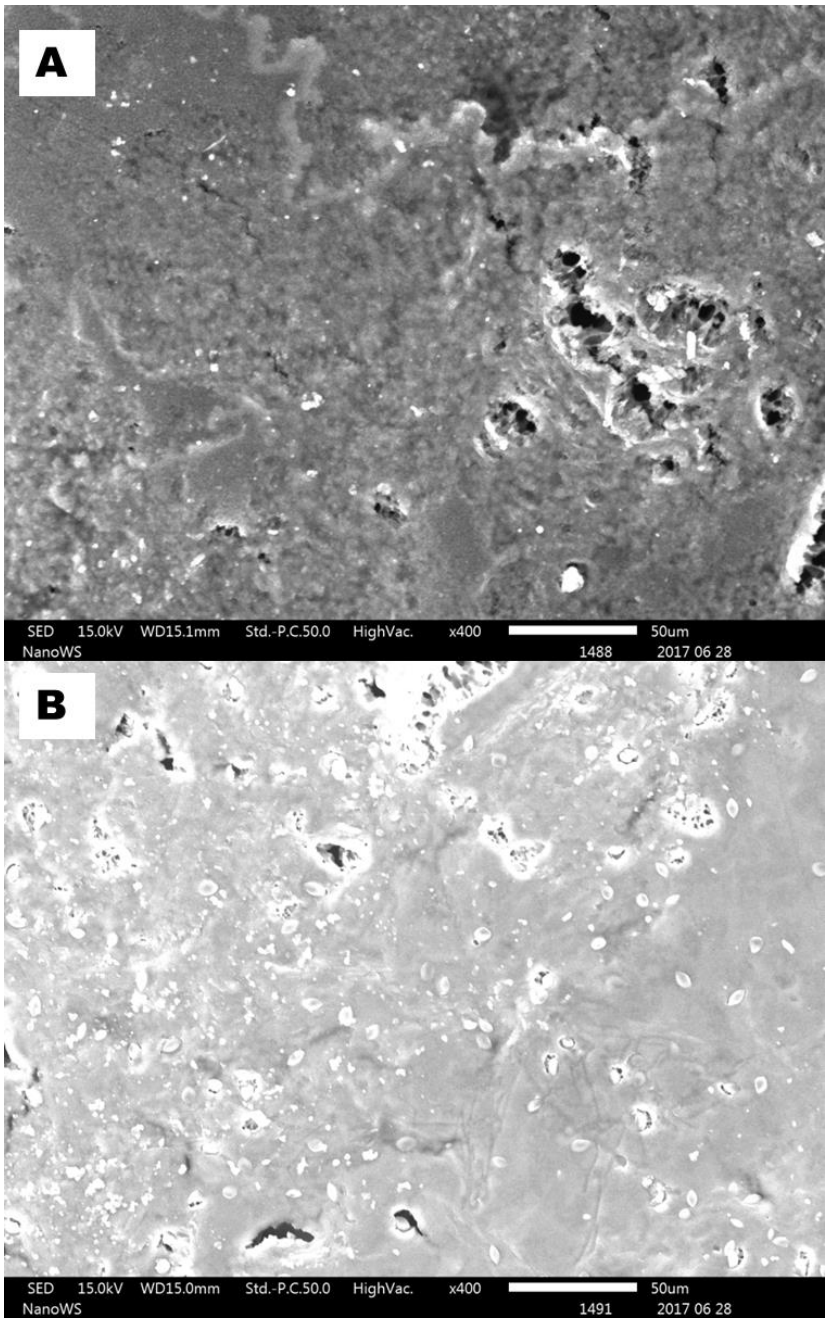


Figure 5.1 SEM images of phase inversion prepared PIMs at different composition ratios. A = 60:30:10 and B = 40:40:20

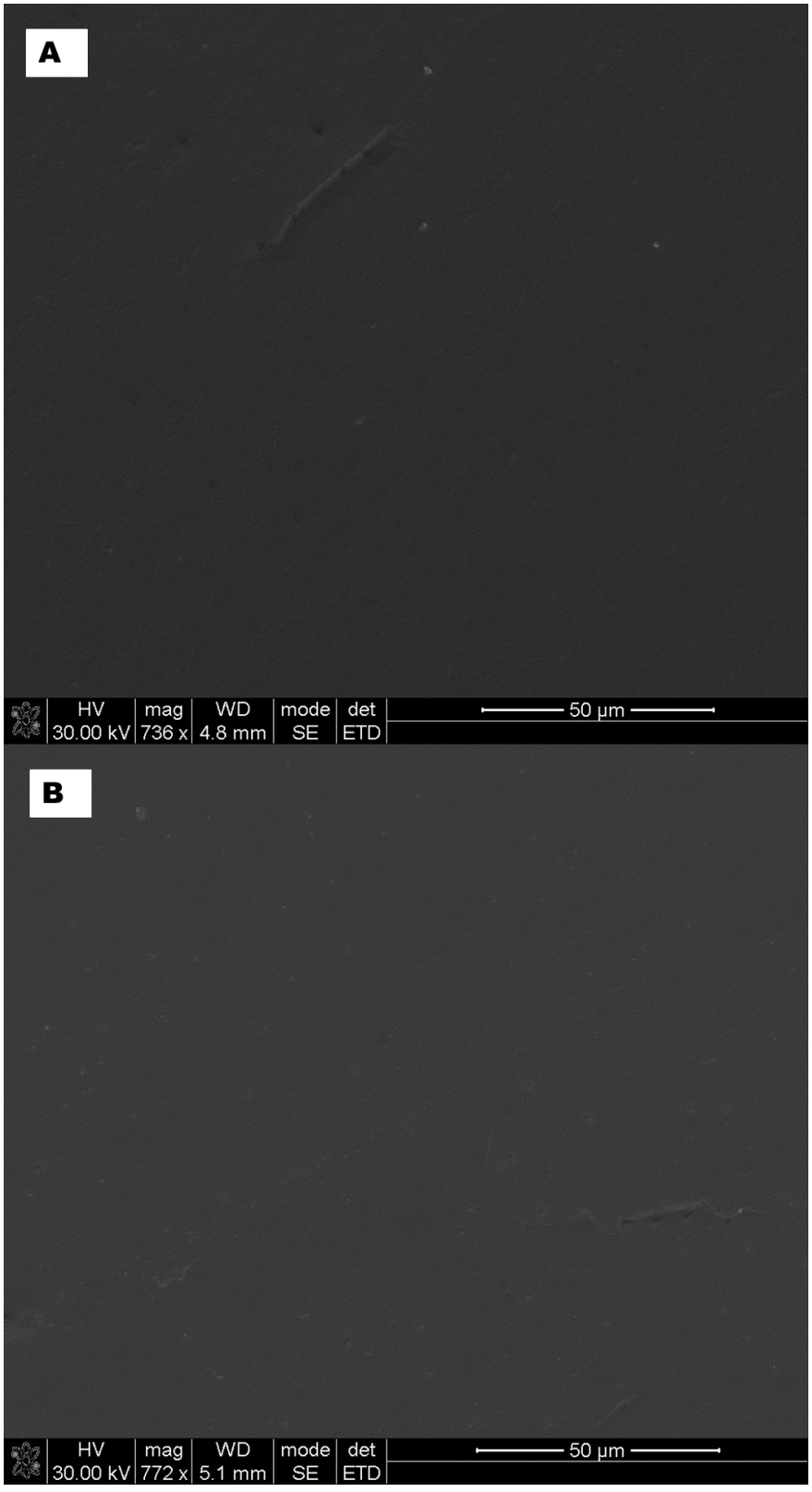


Figure 5.2 SEM images of solvent evaporation prepared PIMs at different composition ratios. A = 60:30:10 and B = 40:40:20

5.2 **Composition ratio optimization**

As stated in the literature review, some carriers like our carrier of choice Aliquat 336 have the ability to function as both carrier and plasticizer (Almeida, Cattrall and Kolev, 2012, 2017; Vázquez et al., 2014). In such cases the use of plasticizer is often deemed unnecessary and due to their high costs synthesizing a plasticizer free membrane is a more cost-effective option. A plasticizer free PSF based PIM was therefore explored.

The best membrane composition weight ratio was investigated by synthesizing six different PIMs. Their mechanical stability and extraction efficiencies were investigated and the membrane composition that produced the desired mechanical stability was used for further studies.

5.2.1 Mechanical stability

As mentioned above, mechanical stability is one of the most vital properties for any membrane. It is therefore important for the membranes to be mechanically stable so they can be utilized for various application purposes. PIMs of varied composition ratios (Table 5.2) were investigated to determine the optimum ratio where the carrier would plasticize the very rigid polysulfone, whilst maintaining its mechanical stability.

Table 5.2 Composition and physical properties of various synthesised PIM membranes

PIM	Polysulfone %	Aliquat336 %	mol L^{-1}	flexibility	Mechanical stability
PIM 0	100	0	0.00	flexible	✓
PIM 1	70	30	0.066	Brittle	×
PIM 2	60	40	0.086	Brittle	×
PIM 3	50	50	0.108	flexible	✓
PIM 4	40	60	0.127	flexible	✓
PIM 5	30	70	0.146	Soft	×
PIM 6	20	80	0.165	Soft	×

Plasticizer free PSF based membranes were successfully synthesized. However, at low carrier concentrations (below 50%) the membranes were stiff, brittle and mechanically unstable. This means that not enough carrier had been added to overcome the intermolecular forces of the polymer. PSF has a very high glass transition temperature of 185ºC meaning it has very strong intermolecular forces and Nghiem (2006) stated that higher intermolecular force strength subjects a membrane to greater rigidity. Thus very high amounts of the carrier would be required to for a polymer of such great rigidity to be plasticized (Nghiem et al., 2006).

It was observed that when the carrier concentration was increased the membrane's flexibility also increased. The desired flexibility was achieved between 50% and 60% ($0.108 - 0.127\ mol\ L^{-1}$) carrier concentration. These membranes appeared white, homogeneous, flexible, and had good mechanical strength.

When the carrier concentration was increased further to 70% ($0.146\ mol\ L^{-1}$), the membranes became viscous, soft and demonstrated poor mechanical stability. Since the carrier has to intercalate itself in between the polymer chains, lengthening the distance between the polymer molecules, resulting in the reduction of strength of the intermolecular forces between the polymer matrixes. Thus decreasing glass transition temperature of the polymer, and consequently increasing the flexibility and softening the membrane.

When the carrier concentration was above 60% ($> 0.127\ mol\ L^{-1}$) the intermolecular forces strength of the membrane dropped to a point where the polymer matrix could no longer successfully entangle due to the distance between the polymer molecules being too wide. Meaning there was too much carrier than the polymer matrix could handle, thus the loss of mechanical stability.

Since membranes that lack mechanical stability are not viable for application; PIM 1, PIM 2, PIM 5 and PIM 6 were not studied further. The control PIM (PIM 0), PIM 3 and PIM 4 presented the desired membrane properties in terms of flexibility and mechanical strength, they were therefore used in further studies.

5.2.2 Extraction efficiency

Permeability of the membranes was investigated by monitoring their extraction capacity of Cr(VI). The preliminary extraction studies were done for PIM 3 with the composition ratio of 50% PSF: 50% Aliquat 336 and PIM 4 with the composition ratio of 40% PSF: 60% Aliquat 336 because they had the desired flexibility and mechanical stability. They were then compared to a control membrane composed of only PSF (PIM 0). In this study the extraction efficiencies of PIMs with carrier concentration above 60% and those below 50% were not investigated due to their lack of mechanical stability.

It was found that on its own PSF can transport the target analyte, obtaining a flux of $2.17 \times 10^{-8}\ mol\ m^{-2}s^{-1}$. This demonstrated that PSF is permeable. This is in agreement with Casadellà, Schaetzle and Loos, (2016) where the control PIM was reported to allow ion transport at slow rates compared to carrier containing membrane. However, it contradicts the observation by Kebiche-Senhadji et al., (2008) and Meng et al., (2017), where in the absence of carrier the membrane prohibits ion transfer from feed to receiver phase. Ladewig and Al-Shaeli, (2017) reported that permeability in solvent evaporation prepared (dense) membranes can only be observed when the polymer is a highly permeable or porous one such as silicon. PSF is hydrophobic and porous in nature. Its porosity enables the membrane to be permeable. However, its hydrophobicity reduces its extraction efficiency. The hydrophobicity causes a repulsive response towards the feed solution. This limits the contact time the membrane surface has with the source solution and thus low permeability. This agrees with O'Bryan *et al.*, 2016 where he stated that the membranes with high glass transition temperatures have higher ion-pair mass transfer diffusive resistance and thus poor permeability rate (O'Bryan et al., 2016)

Figure 5.3 shows that when the carrier was introduced, an increase in extraction efficiency of the PIMs was observed. The carrier acts as a facilitator for ion-exchange between feed and receiver solution. Thus, the introduction of a carrier resulted in an increase in the membrane permeability. PIM 3 achieved a flux of $4.86 \times 10^{-8}\ mol\ m^{-2}s^{-1}$ which is two folds higher than that of PIM 0.

A further increase in the carrier concentration resulted in faster ion exchange. This is attributed to both the plasticizing nature of the carrier Aliquat 336 and its facilitation of ion-exchange. The higher the carrier concentration the more ions available to transport the analyte from the feed phase to the receiver phase. Higher carrier concentrations also increase the flexibility of the membrane, which is a consequence of a lower glass transition temperature. This means that the ion-pair mass transfer diffusive resistance decreases resulting in faster ion-exchange and thus better permeability rate.

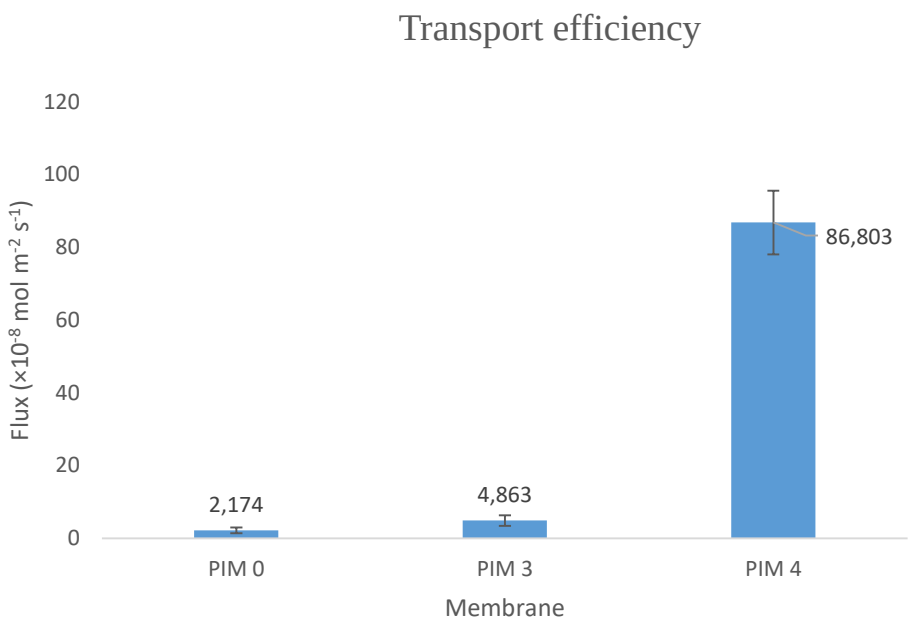


Figure 5.3 Extraction efficiency of Cr (VI) by PIM with different carrier concentrations

The highest permeability was observed at PIM 4, having a flux of $8.68 \times 10^{-7}\ mol\, m^{-2} s^{-1}$. This makes PIM 4 (40% PSF: 60% Aliquat 336) the optimal composition weight ratio, with an extraction efficiency of 17 folds higher than PIM 3 and about 40 folds higher than that of PIM 0.

5.3 Stability studies

A PIM needs to have both mechanical and chemical stability. Chemical stability is dictated by its ability to effectively entrap carrier into its polymer matrix with minimum leaching to its surrounding solutions during application. Its behaviour in different environmental conditions is an important parameter to consider when choosing the PIM parameters for an application due to the different physical and chemical properties each component is associated with. The stability of a PIM on certain environmental conditions can therefore be quantified by monitoring its weight loss when exposed to that condition.

The stability of the PSF based PIM at optimum composition ratio of 40% PSF and 60% Aliquat 336 and different membrane thicknesses was investigated. This was done in both acidic (1 M HNO_3) and basic conditions (0.05 M NaOH). This was done by measuring the weight of the membranes before and after they were immersed in the 0.05 M NaOH and 1 M HNO_3 solutions. The average mass percentage lost after exposure are presented in Figure 5.4.

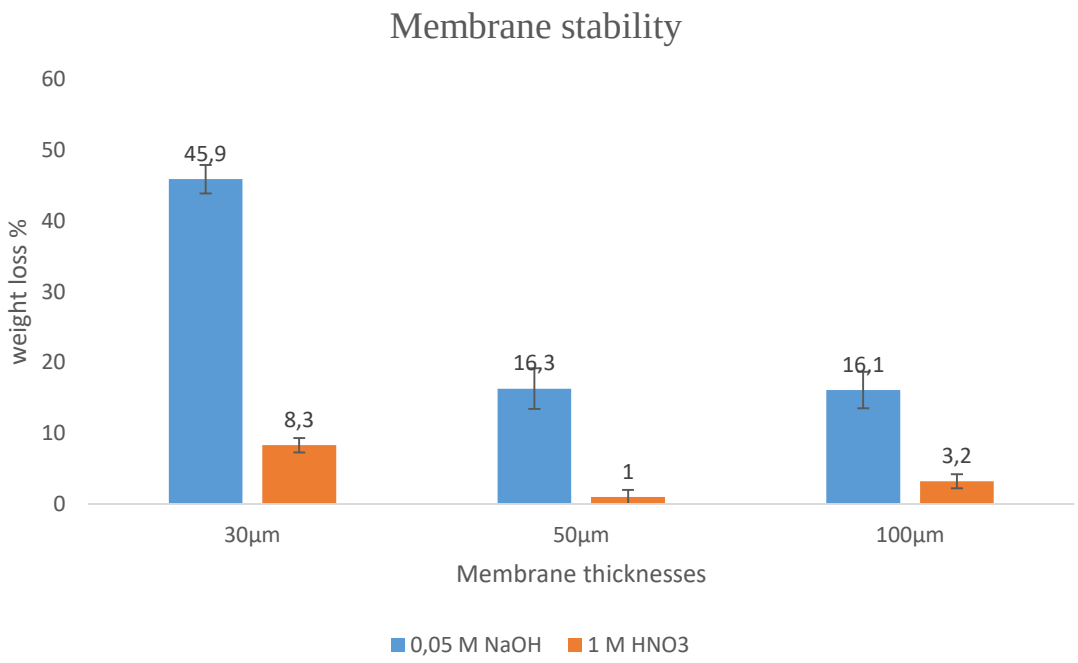


Figure 5.4 chemical stability of PIMs at different membrane thicknesses in acidic and basic conditions

It was observed that all the membranes at different thicknesses were more stable in the acidic conditions compared to the basic conditions. This could be attributed to the positive charge of the carrier Aliquat 336 which enable an interaction between the highly concentrated hydroxide (OH^-) anions from the NaOH and thus that activity exposes the carrier which then results in it leaching out of the membrane. In the acidic solution there is a high presence of hydronium cations (H_3O^+) and since Aliquat 336 is also cationic there will be very minimal interaction and thus the higher stability of the PIM.

At 30 µm membrane thickness the PIMs were at their most unstable, losing an average of 45.9% of their original mass on basic solution and an average of 8.3% on the acidic solution. This could be due to the membrane being too thin, leaving very little room for the carrier to travel which then maximizes the interaction between the carrier and the surrounding solutions, this makes the membrane more prone to leaching and thus the loss of its mechanical stability. There was an increase in the membrane stability with an increase in thickness. This observation is in agreement with the results obtained by Schow (1996) (Schow, Peterson and Lamb, 1996). Between the membrane thicknesses of 50 µm and 100 µm, no significant difference was observed in their stability. They both lost respectively 16.3% and 16.1% on the basic solution and 1% and 3.2% in the acidic solution This is however significantly lower than the results obtained for the PIMs of 30 µm thickness. Thus membranes become more stable at higher thicknesses.

5.4 **Characterization**

5.4.1 FTIR

The FTIR technique was used to investigate the presence of polysulfone and Aliquat 336 functional groups on the synthesized polysulfone based polymer inclusion membrane. This was done by recording the absorption spectra of PSF, Aliquat 336 and that of the PIM. The polysulfone has a number of different functional groups. The following functional groups O-S-O, C-O-C, C-C aromatic and –CSO_2C- were observed at the absorptions wavenumbers of 1147.54 cm^{-1}, 1244 cm^{-1}, 1583.52 cm^{-1} and 1322.49 cm^{-1} respectively (see Figure 5.5) this is in agreement with the results reported by Singh et al., (2014). The Aliquat 336

functional groups C-H and –N-CH_3 absorbed at 2954.81 cm^{-1} and 1465.95 cm^{-1} respectively (see Figure 5.6).

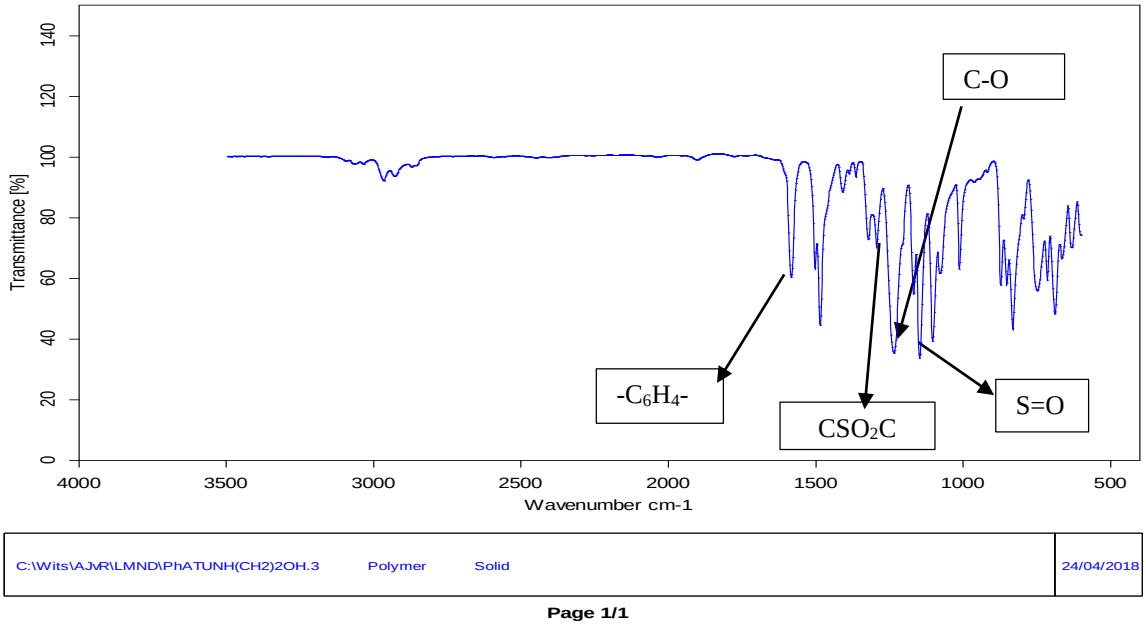


Figure 5.5 FTIR spectra of Polysulfone

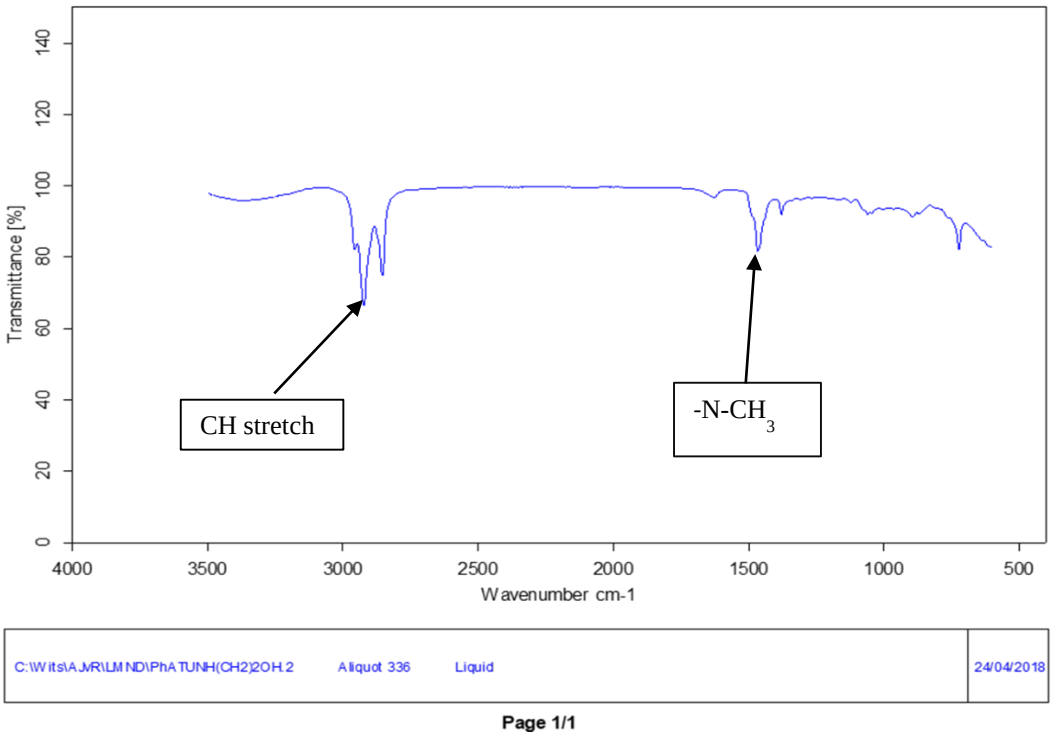


Figure 5.6 FTIR spectra of Aliquat 336

The main PSF functional groups were observed on the PIM IR spectra as shown in Figure 5.7. The sulfone group S=O symmetric stretch was observed at 1148.70 cm^{-1}, followed by the C-O stretch at 1238.24 cm^{-1}, then the $–CSO_2C-$ at 1322.28 cm^{-1} and lastly the aromatic ring stretch at 1584.30 cm^{-1}. The presence of Aliquat 336 functional groups was also observed at 1467.31 cm^{-1} due to the $–N-CH_3$ and at 2955.48 cm^{-1} and 2854.69 cm^{-1} due to CH stretch.

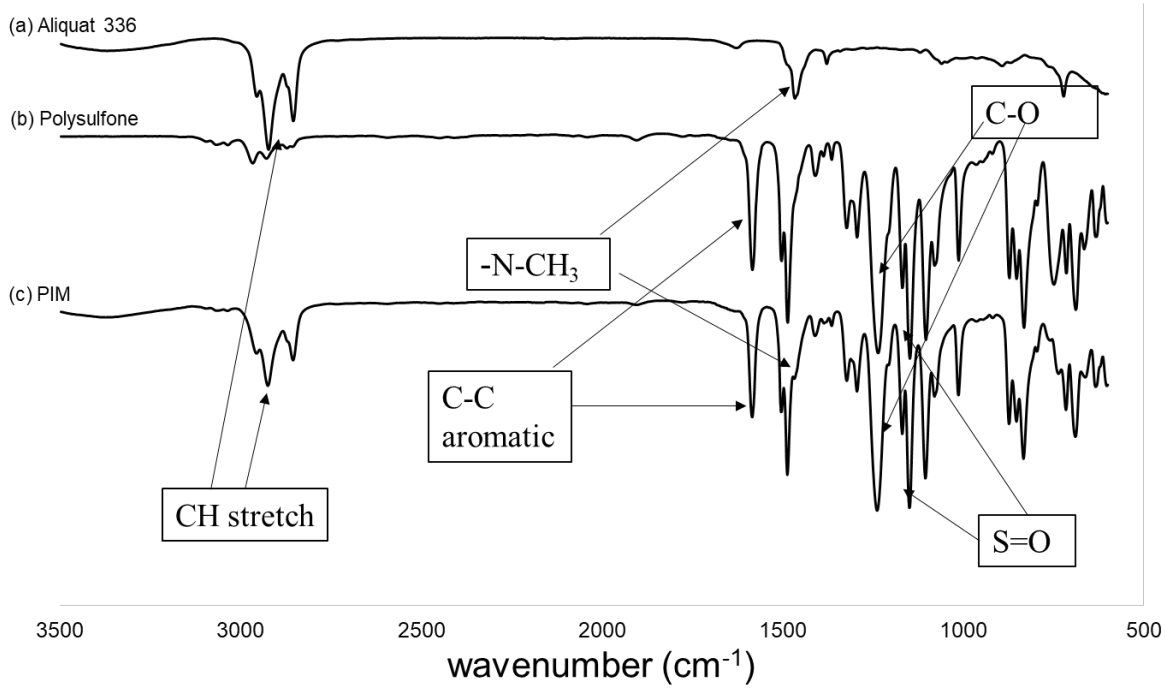


Figure 5.7 FTIR spectrums (a) Aliquat 336 (b) Polysulfone (c) PIM

The presence of the functional groups of both compounds in the IR spectra confirmed that the PIM was indeed composed of both PSF and Aliquat 336. This also suggests that during membrane synthesis only physical interactions occurred between the two components. It can therefore be concluded that the membrane's mechanical stability is solely dependent on the weak physical interactions and thus, the polymer chains act as a support for the carrier's liquid domains.

5.4.2 Surface characteristics

To identify the surface morphology of the membranes, SEM and AFM analysis was done for flexible PIMs (PIM 0, PIM 3 and PIM 4). The SEM images can be observed on the figures below (Figure 5.8, Figure 5.9 and Figure 5.10)

All three membranes were dense; thus no pores were observed. This is in agreement with Ladewig and Al-Shaeli, (2017), where it was reported that the membrane morphology is highly dependent on the method of preparation and dense membranes are to be observed when the solvent evaporation method is used. The control membrane PIM 0 (Figure 5.8) had a featureless, smoother surface relative to the other PIMs. On the other hand both PIM 3 (Figure 5.9) and PIM 4 (Figure 5.10) had randomly distributed liquid microdomains of the carrier Aliquat 336 on the membrane surface.

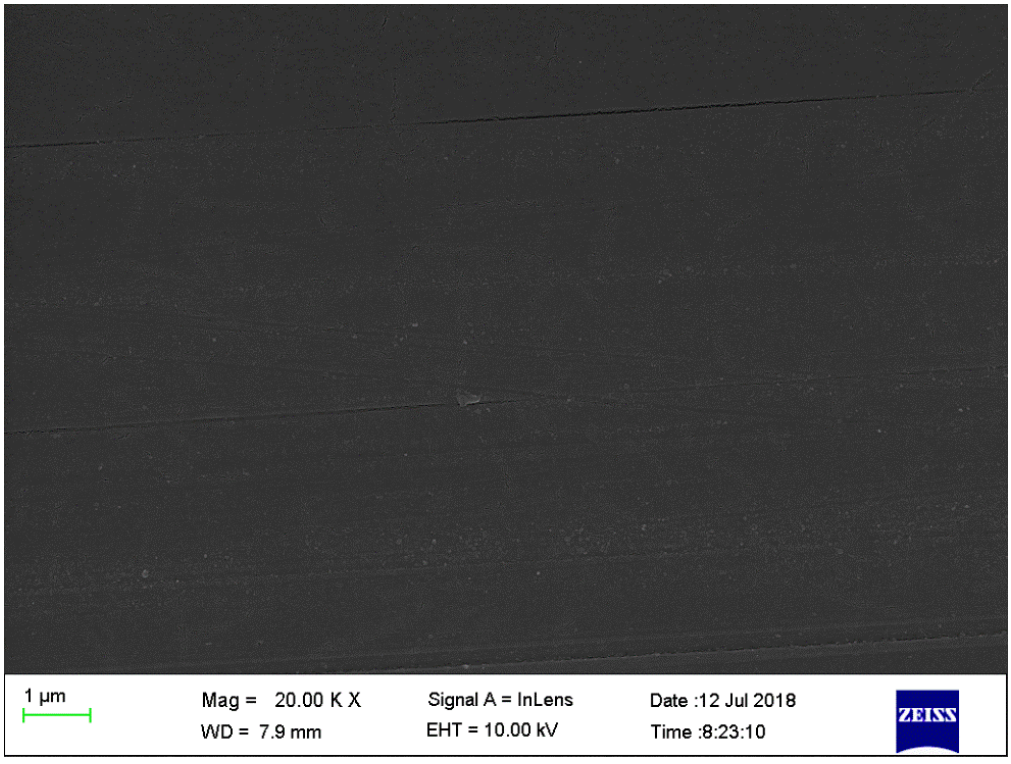


Figure 5.8 SEM image of the control PIM, PIM 0 (100% PSF)

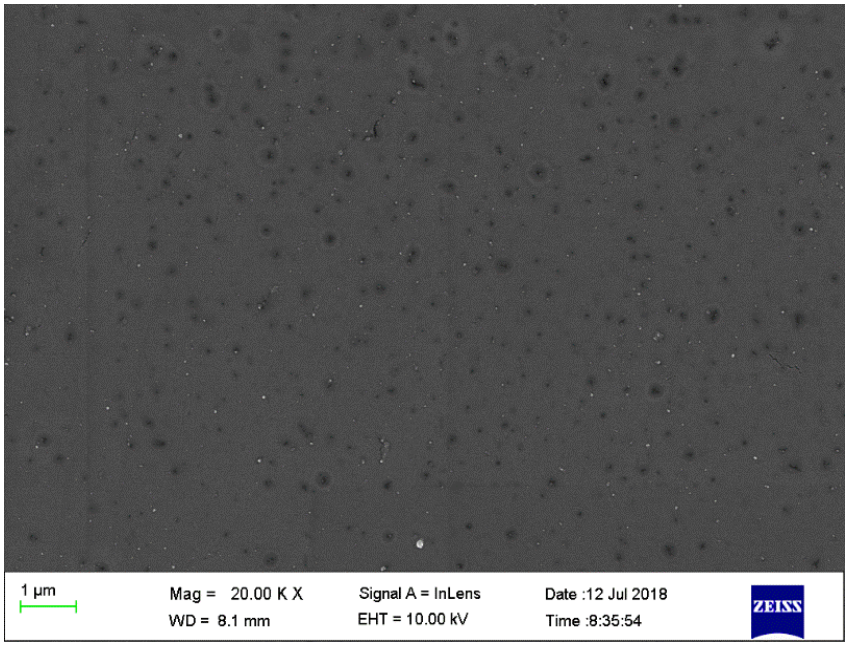


Figure 5.10 SEM image of PIM 3 (50% PSF: 50% Aliquat 336)

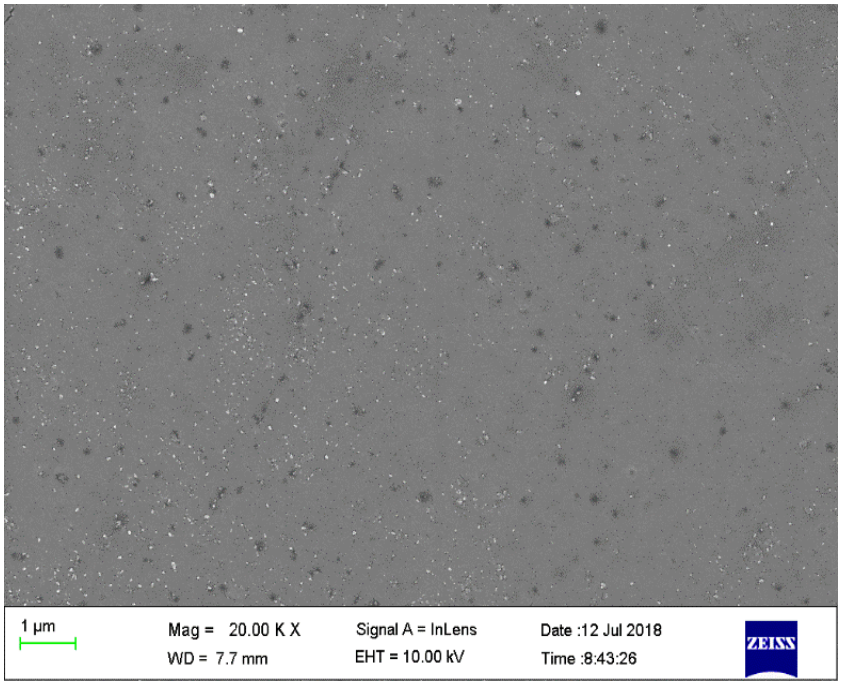


Figure 5. 9 SEM image of PIM 4 (40% PSF: 60% Aliquat 336

AFM analysis was carried out to investigate the roughness of the membrane surfaces. Three dimensional (3D) images of the PIM surfaces can be observed at Figure 5.11 and roughness analysis at Figure 5.12. An increase in roughness was observed with an increase in carrier concentration (see Figure 5.13). This could be

attributed to the carrier interacting with the polymer matrix creating alternating liquid domains. An increase in carrier therefore increases the liquid domain regions and thus a rougher surface. Gherasim et al., (2011), reported that the microdomains function as liquid pores that are responsible for facilitating transport in the PIM. This therefore agrees with the observed increase in permeability with an increase in carrier concentration.

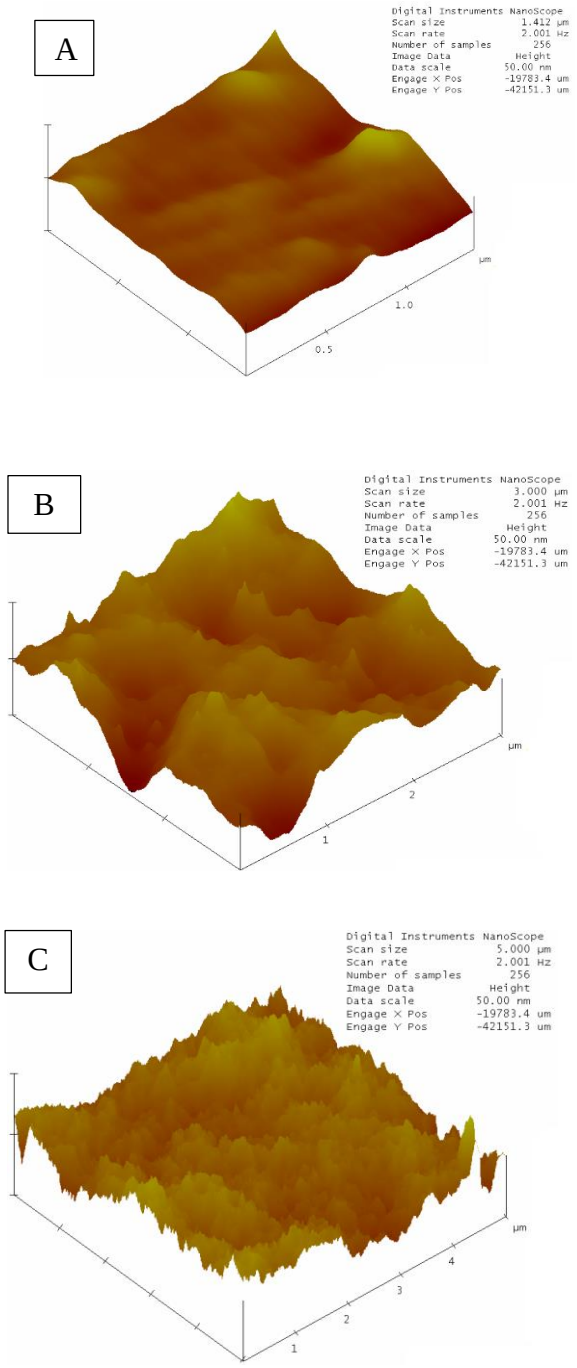


Figure 5.11 Three dimensional (3D) images of the PIM surfaces. A = PIM 0, B = PIM 3 and C = PIM 4

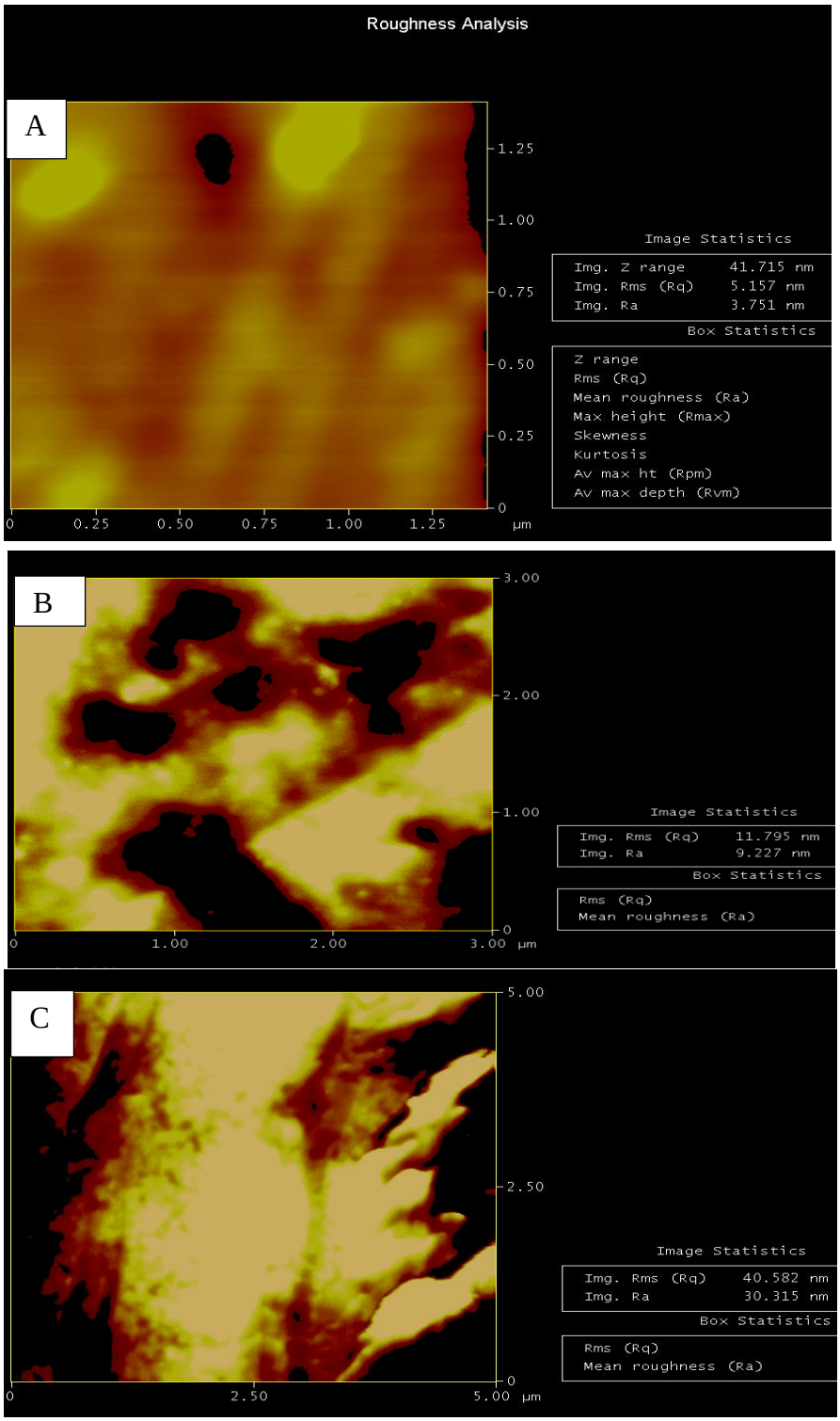


Figure 5.12 AMF roughness analysis images of the PIMs. A = PIM 0, B = PIM 3 and C = PIM 4

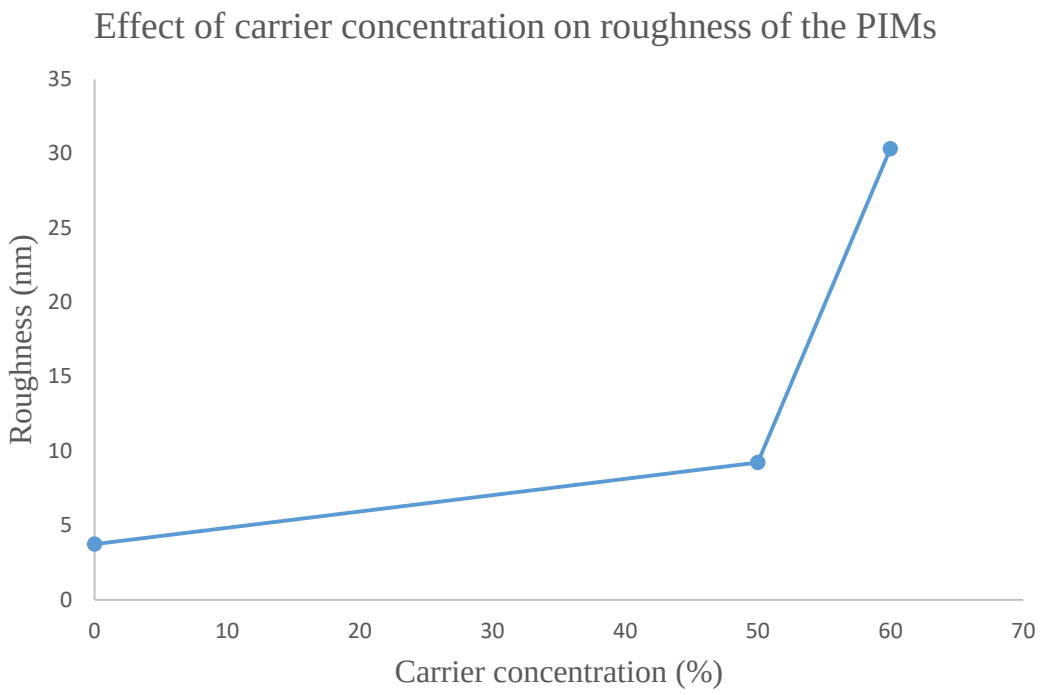


Figure 5.13 A graph representation of the effect of carrier concentration on roughness of the PIMs

5.4.3 Contact angle

Hydrophilicity of the membrane surface at different carrier (Aliquat 336) concentrations was investigated by measuring their contact angle. For the membrane to function effectively it needs to have a balance of its hydrophilicity. When a membrane is too hydrophobic it is prone to low extraction efficiencies and biofouling; when it is too hydrophilic it will dissolve in the water, leaching out the carrier. Therefore, the PIM must be hydrophobic enough for the carrier to not leach out and hydrophilic enough to maximize contact time between membrane surface and feed solution.

Figure 5.14 shows the average contact angle values for the different PIMs. PIM 0 had the highest value of 90.76º, suggesting that polysulfone is hydrophobic in nature. When carrier was introduced a decrease in contact angle was observed, meaning hydrophilicity increases with an increase in carrier concentration. This resulted in an increase in contact time between the PIM and the feed solution and

thus increasing extraction efficiency. PIM 3 and PIM 4 had average contact angle of 48.75º and 34.00º respectively. This decrease in contact angle is in agreement with the extraction results. PIM 4 had the lowest contact angle meaning it has the highest contact time and thus the largest extraction capacity.

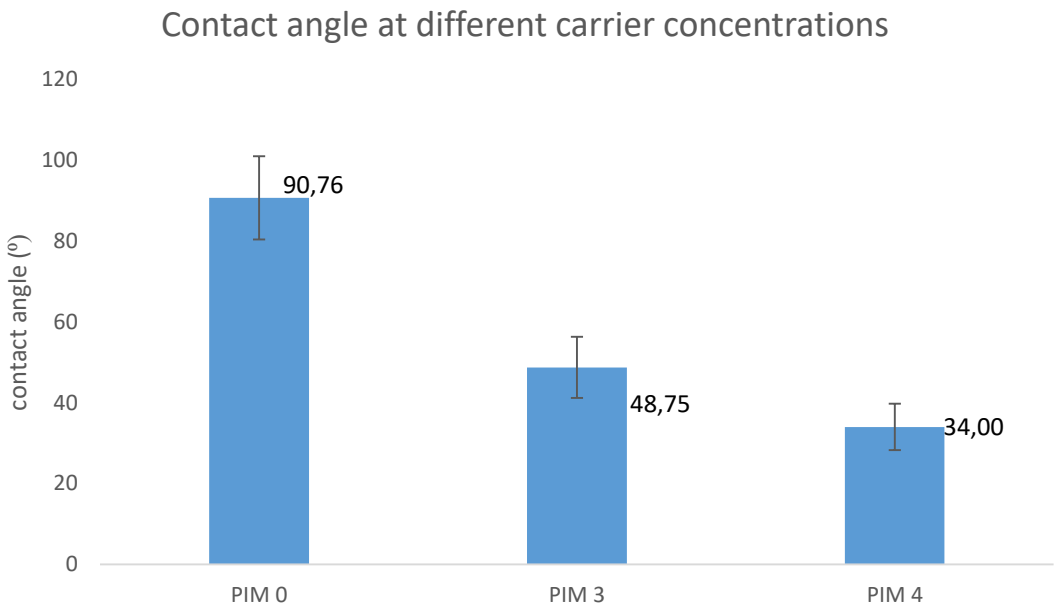


Figure 5.14 Water contact angle of PIM with different carrier concentrations

5.4.4 Thermal stability

TGA analysis was done to investigate the thermal stability of the control membrane (PIM 0), PIM 3 and PIM 4. This was done by observing the weight loss of polysulfone and the PIMs at different carrier concentrations as the temperature increases. The thermogram curves are shown in Figure 5.15.

Polysulfone is thermally stable up to 500 °C where its thermal degradation occurs, losing about 64% of its original weight. PIM 3 and PIM 4 have the same degradation pattern. A minor mass loss was observed before 100 °C, this was attributable to the evaporation of the solvent and moisture that remained in the membrane matrix during synthesis. They are both stable until the temperature of about 180 °C where they start degrading, losing the carrier. This indicates that the PIMs are stable at

standard operating temperatures (≤45 ºC). PIM 4 has higher carrier concentration, hence the larger weight loss. It can be observed that the polysulfone degrades at the same temperature for all 3 membranes. This means that the polymer matrix is not chemically disturbed by the presence of carrier in the membrane.

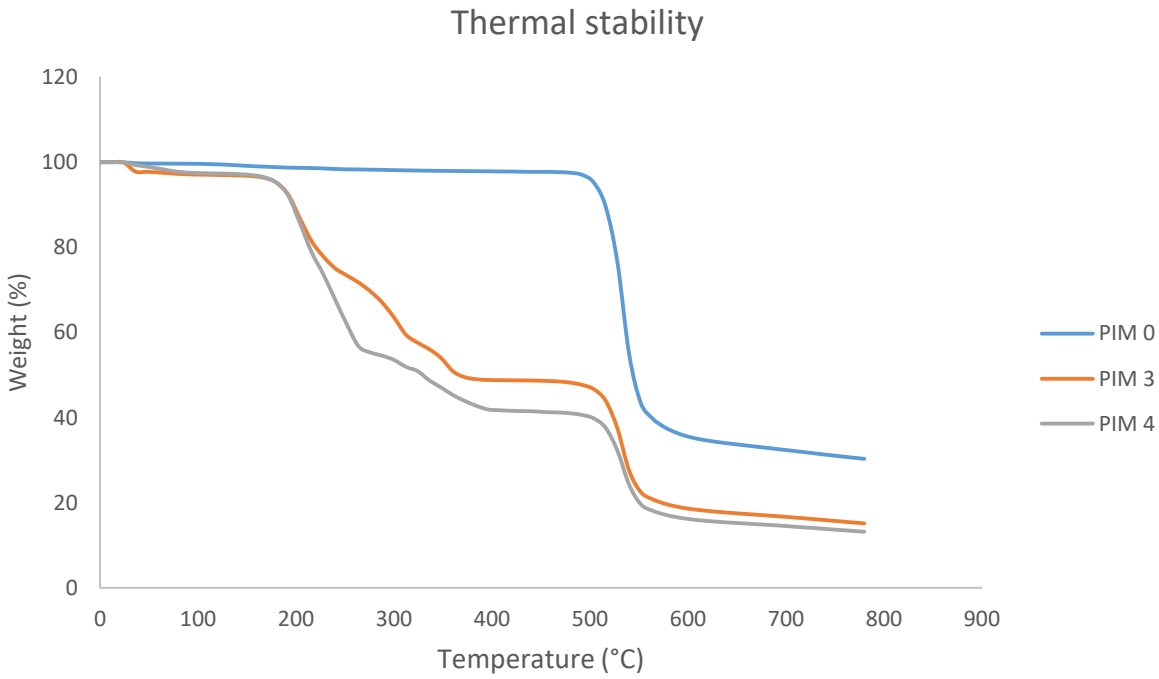


Figure 5.15 Thermograms of PIM 0, PIM 3 and PIM 4

5.5 **Comparison studies**

As stated in the literature review poly(vinyl chloride) (PVC) is one of the most commonly used base polymers for preparation of PIMs. However, its instability under basic conditions brought about the need to explore other base polymers that will overcome such limitations. Polysulfone (PSF) was then investigated. A comparison study was conducted between the PSF based PIMs and the PVC based PIMs. This was done to determine if PSF can outperform PVC as a base polymer.

5.5.1 Mechanical stability and permeability

The optimum membrane composition weight ratio of PVC based PIMs was investigated. The mechanical stability and permeability of the PIMs was then

compared with those obtained for PIM. The different mechanical stability of the PVC based PIMs is detailed in Table 3.

Mechanical stability of the PVC based PIMs was observed between 20% and 40% carrier concentration. Below 20% the control PIM, PIM 7 (100% PVC) was stiff and brittle. When carrier concentration was increased above 40% the membranes lost their mechanical stability and became soft and sticky. This could be attributed to the saturation of the base polymer with the carrier therefore at higher concentration of the carrier, over plasticization occurs thus making the polymer mechanically unstable. The PSF based PIMs only lost their mechanical stability at carrier concentrations above 60%, they were mechanically stable between 50% and 60% carrier concentration. The PVC requires less carrier concentration than the PSF to reach oversaturation of the polymer matrix and thus producing a mechanically unstable membrane. This is due to the difference in glass transition temperature (Tg), PSF has a Tg value of 185ºC and PVC has a Tg of about 80°C. This means that PSF has stronger intermolecular forces relative to PVC, therefore it will require much higher carrier concentrations to overcome its very rigid nature.

Table 5.3 Effect of varying PVC and Aliquat 336 concentration on flexibility and stability

PIM	PVC	Aliquat 336	Flexibility	Mechanical stability
PIM 7	100	0	Stiff	×
PIM 8	80	20	flexible	✓
PIM 9	70	30	flexible	✓
PIM 10	60	40	flexible	✓
PIM 11	50	50	soft	×
PIM 12	40	60	Soft	×

The rate of permeation of the mechanically stable PVC based PIMs was investigated by determining their flux of Cr(VI). The preliminary study was done for PIM 8 (80% PVC: 20% Aliquat 336), PIM 9 (70% PVC: 30% Aliquat 336) and PIM 10 (60% PVC: 40% Aliquat 336) and then compared to the flux of the

mechanically stable PSF based PIMs, PIM 0 (100% PSF), PIM 3 (50% PSF: 50% Aliquat 336) and PIM 4 (40% PSF: 60% Aliquat 336).

In the PVC based PIMs, PIM 8 with 20% carrier concentration showed the lowest flux. When carrier concentration was increased to 30%, an increase in the flux was also observed. The highest permeability was observed at PIM 10 where an average flux of $305 \times 10^{-8}\ mol\ m^{-2}\ s^{-1}$ over the 3 h period hereby making the 60% PVC and 40% Aliquat 336 the optimal compositional ratio for the extraction. Similar to the PSF based PIMs an increase in permeability of the PIMs was observed with an increase in carrier concentration.

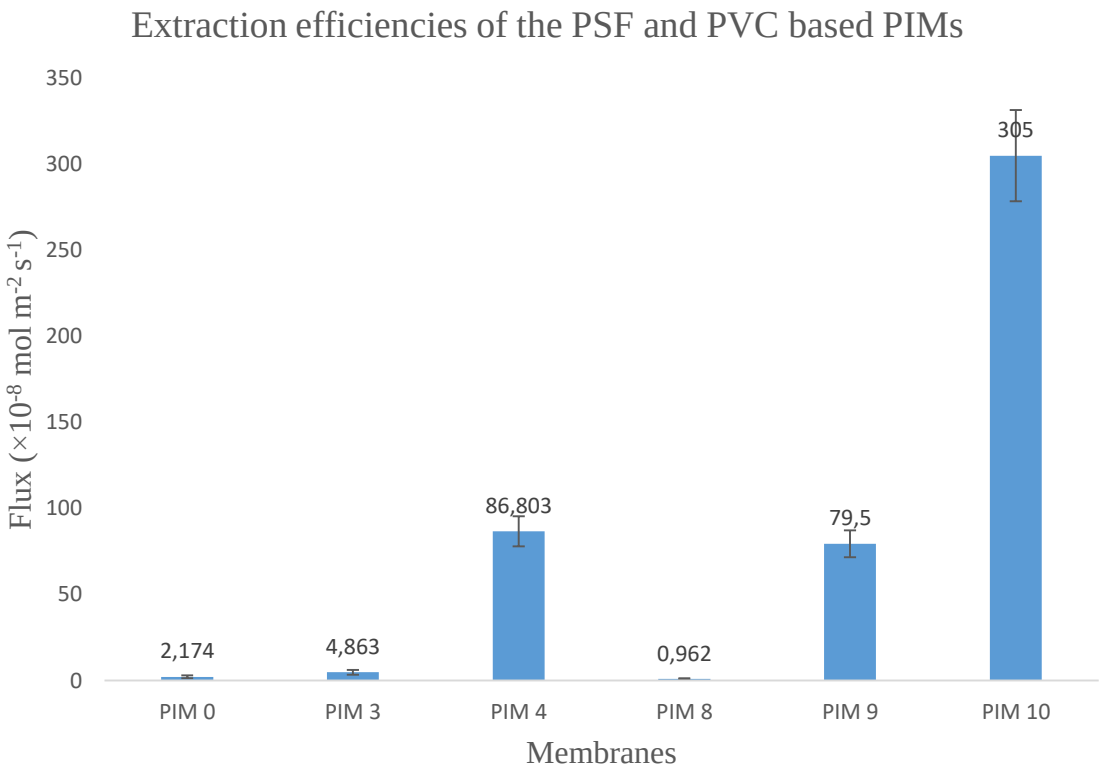


Figure 5.16 Extraction efficiency of Cr (VI) by PSF and PVC based PIMs at different carrier concentrations

The PSF control PIM, PIM 0 had the lowest transport efficiency in the PSF based PIMs, exhibiting an average flux of $2.174 \times 10^{-8}\ mol\ m^{-2}\ s^{-1}$. This was however twice that of PVC base PIM, PIM 8 with a value of $0.962 \times 10^{-8}\ mol\ m^{-2}\ s^{-1}$

meaning the PSF control PIM has better performs better than PVC based PIMs in transporting Cr across the membrane when the carrier concentration was ≤20% Aliquat. The optimum compositional ratio for the PSF membrane was found to be PIM 4 with a carrier concentration of 60% and a flux of $86.80 \times 10^{-8}\, mol\, m^{-2}\, s^{-1}$, these was significantly low compared to that of PVC based PIM optimum (PIM 10), with an average flux of $305 \times 10^{-8}\, mol\, m^{-2}\, s^{-1}$.

The optimum PVC based PIM had a flux more than threefold higher than that of the PSF based PIM optimum, even though the PSF PIM had higher carrier concentration. This could be attributed to their wettability. Wettability refers to the propensity of a liquid to spread across a solid and this process can be measured in terms of contact angle where such wetting can be total, partial and non-wetting (Kumar and Prabhu, 2007). The lower the contact angle means higher hydrophilicity and thus proper interaction between the aqueous liquid and the membrane surface. This agrees with the contact angle values obtained for the PSF based PIMs (Figure 5.14) where the optimum PIM had the highest hydrophilicity at a contact angle value of 34º. Although actual values of the contact angle of PVC varies across different solutions, reports have shown that PVC has a lower water contact angle than PSF (Fan et al., 2014). In a study Vázquez et al., (2014) demonstrated that the of Aliquat 336 results in an increase in hydrophilicity of a membrane surface. When 9% of Aliquat 336 was added the PIM's surfaced went from hydrophobic with a value of 86º to hydrophilic at 28º contact angle. This is evidence that PVC is more hydrophilic even at low carrier concentration values and thus the higher permeability compared to PSF based PIM even though it had lower carrier concentration.

5.5.2 Stability studies

The behaviour of a PIM in different environmental conditions is an important parameter to consider when choosing a PIM for an application due to the different physical and chemical properties associated with the PIMs components. The chemical stability of PVC based PIMs and PSF based PIMs was investigated. The thickness of both PIMs was kept at 50 µm. It was observed that both PVC and PSF are highly in acidic conditions with the PSF based PIM losing 1% of its original

mass and the PVC based losing 1.8%. However, under basic conditions both PIMs are less stable than they are in the acidic conditions. The PSF based PIM is more chemically stable in basic conditions than the PVC based PIM. IT lost about 16% of its original mass, whilst the PVC based PIM lost more than 30% of its original mass. The instability of the PVC in basic conditions is due to a dehalogenation reaction occurring within the polymer matrix. Since PVC is a chloroethene organochloride, there is a tendency for the poly(chloroethene) to undergo dehydrochlorination with a base in the presence of a quaternary ammonium (Aliquat 336) (Kise, 1982; Yoshioka *et al.*, 2008).

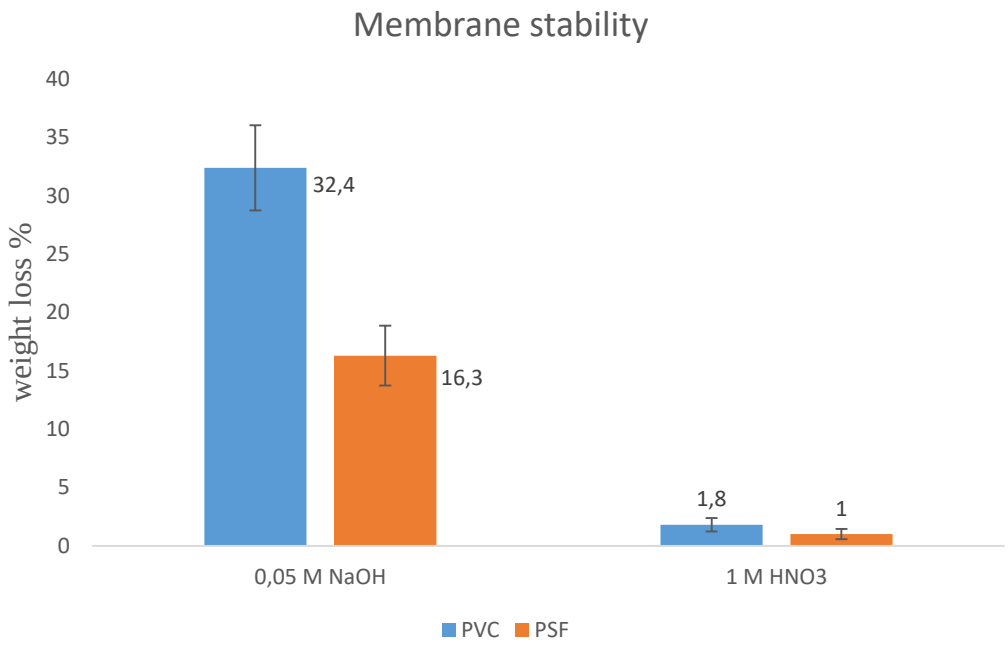


Figure 5.17chemical stability of PIMs composed of different base polymers in acidic and basic conditions

The general mechanism for dehydrohalogenation is shown in Eqn 2. This reaction is initiated by the hydroxide ions binding to the hydrogen atoms of the β-carbon and stripping it away from its original binding site in the carbon atom. The reaction then propagates with the spontaneous release of the chloride ion to form a stable ethane complex. As a consequence, the membrane degrades and loses its mechanical stability.

$$CH_3 - CH_2Cl + NaOH \longrightarrow CH_2 = CH_2 + NaCl + H_20 \qquad (2)$$

The result of the dehydrogenation reaction will yield NaCl and H2O

The instability of the PVC in the NaOH was also observed by the change in coloration of the PVC membrane from transparent to black. The PSF based membrane is seen to be considerably stable in the basic condition, unlike PVC. The better stability observed is a result of the absent of halogens in its molecular structure which are responsible for dehydrohalogenations in PVC, PSF is rather composed of aromatic groups and sulfonyl groups which are not decomposed by bases. The chemical and mechanical stability of PSF can also be attributed to the aromaticity existing within the polymers and also due to the positioning of the groups holding the aromatic compounds in para positions (Rose, 1974). This base stability of PSF gives it an edge in applications or environmental conditions that requires basic conditions.

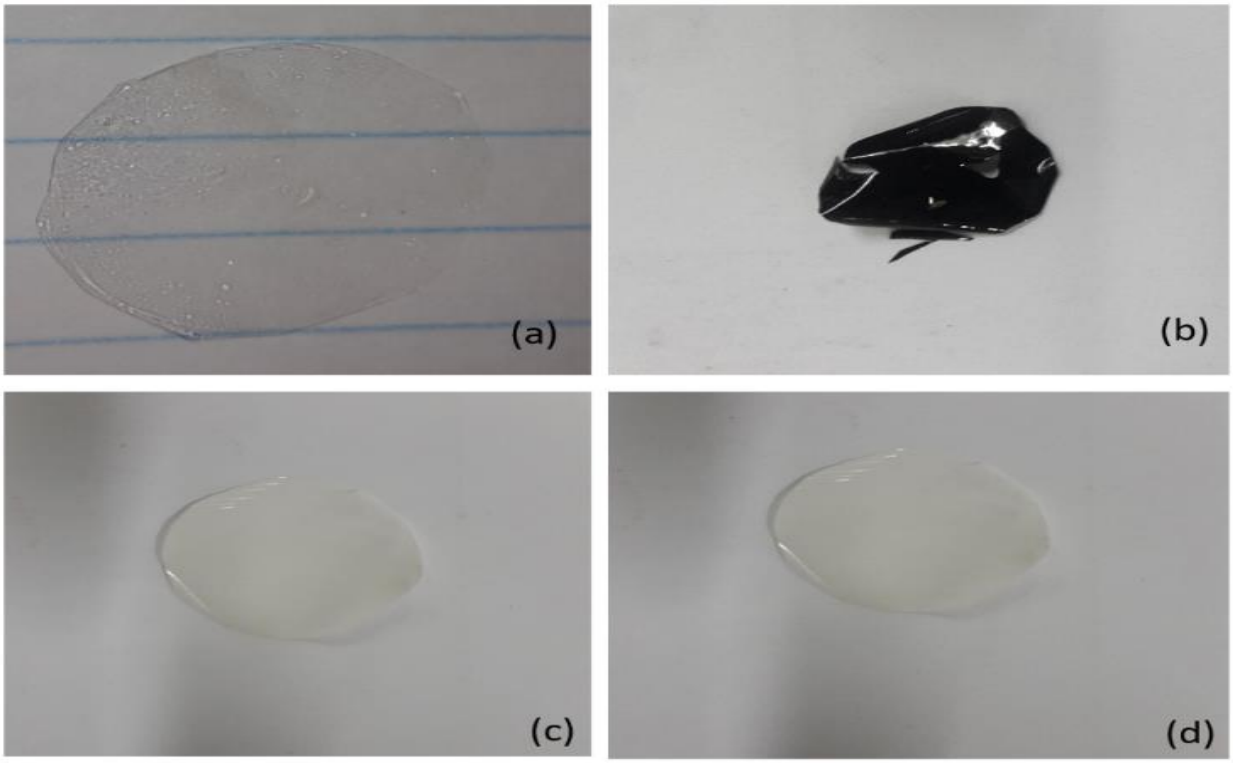


Figure 5.18 (a) image of PVC before base stability experiment, (b) image of PVC after base stability experiment, (c) image of PSF before base stability experiment, (d) image of PSF after base stability experiment

Chapter 6

This chapter states the conclusions of the study

6 Conclusion

In this work, novel polysulfone based PIMs were successfully synthesized using the solvent evaporation technique. The PIMs did not contain plasticizer with Aliquat 336 acted as both carrier and plasticizer.

The optimum PIM (PIM 4) was found to be chemically stable in both acidic and basic mediums as well as temperatures as high as 180 ^{0}C. This indicated that the PIMs are applicable at a wider range of environmental conditions. The thickness of the PIM played a significant role in its stability with a 50 µm and above found to produce chemically stable membranes. PSF based PIMs had a significantly low extraction efficiency compared to the PVC based PIMs. However, they had the advantage of overcoming the stability issues associated with PVC based PIMs under basic conditions.

The characterization results confirmed that the PIMs were dense, hydrophilic and rough on the surface with only physical interactions existing between the carrier and the polymer matrix.

The results obtained in this study indicate that polysulfone can be used as a base polymer for PIMs and the absence of plasticizer makes the polysulfone based PIM more cost effective.

Chapter 7

This chapter states the recommendations for future work

7 Recommendations for future work

Studies that are currently underway as well as those that are planned are listed below;

- How the polysulfone based polymer inclusion membrane's transport efficiency could be improved

- Effects of plasticizer on the membrane's transport efficiency

- Use of more environmentally friendly solvent for membrane preparation

- The reusability and durability of the membrane

- The membrane's selectivity and sensitivity with and without plasticizer

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Appendix A

Stability test on basic medium

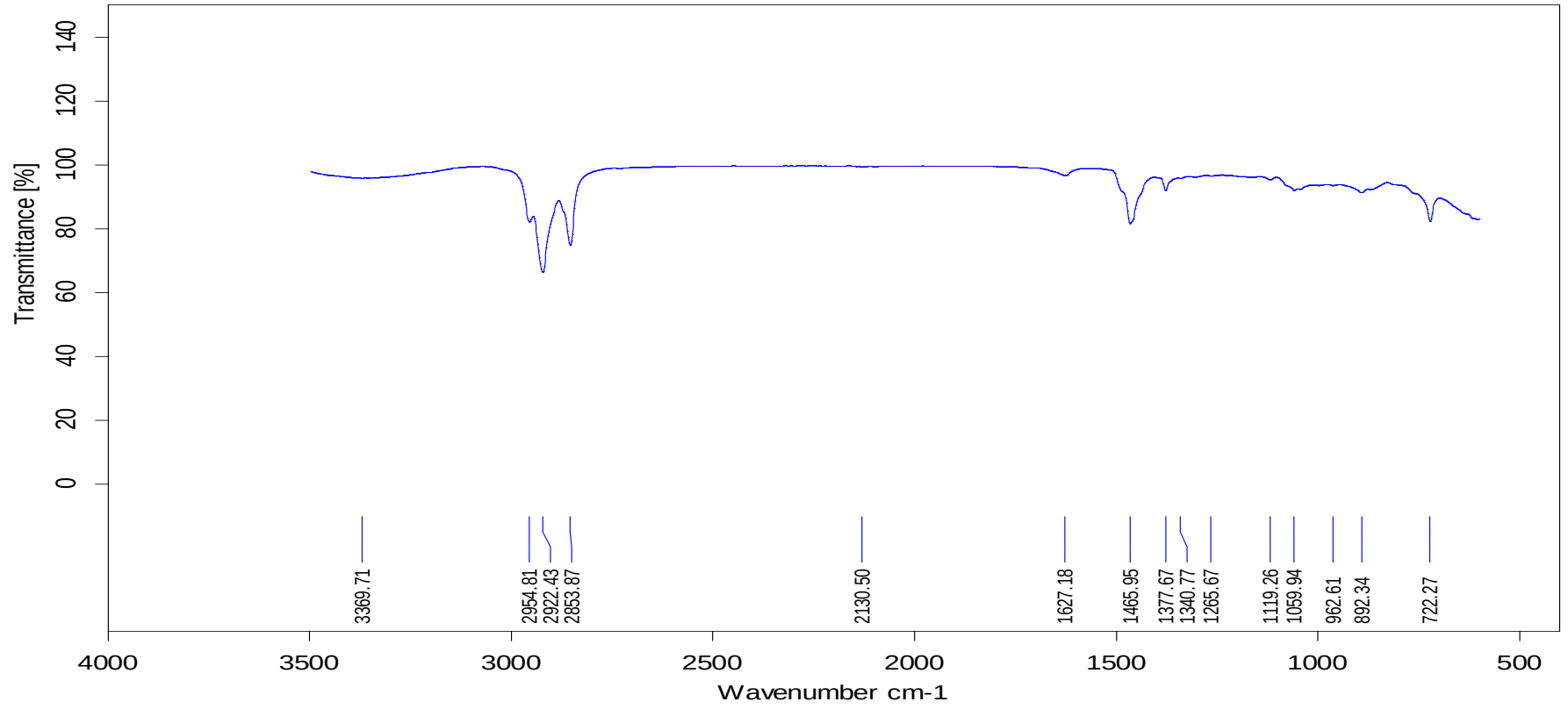
	30µm			50µm			100µm		
	before	after	Mass loss (%)	before	after	Mass loss (%)	before	after	Mass loss (%)
	10,90	5,70	47,71	26,00	22,00	15,38	41,60	36,60	12,02
	11,20	6,30	43,75	25,10	21,50	14,34	34,50	27,00	21,74
	11,90	6,40	46,22	22,90	18,50	19,21	39,40	33,70	14,47
Average	45,89			16,31			16,08		
standard deviation	2,00			2,57			5,06		

Stability test on acidic medium

	30µm			50µm			100µm		
	before	after	Mass loss (%)	before	after	Mass loss (%)	before	after	Mass loss (%)
	17,00	15,90	6,47	24,70	24,50	0,81	39,70	39,00	1,76
	19,80	17,50	11,62	26,20	26,00	0,76	49,80	47,30	5,02
	17,50	16,30	6,86	25,80	25,40	1,55	43,10	41,90	2,78
Average	8,31			1,04			3,19		
standard deviation	2,87			0,44			1,67		

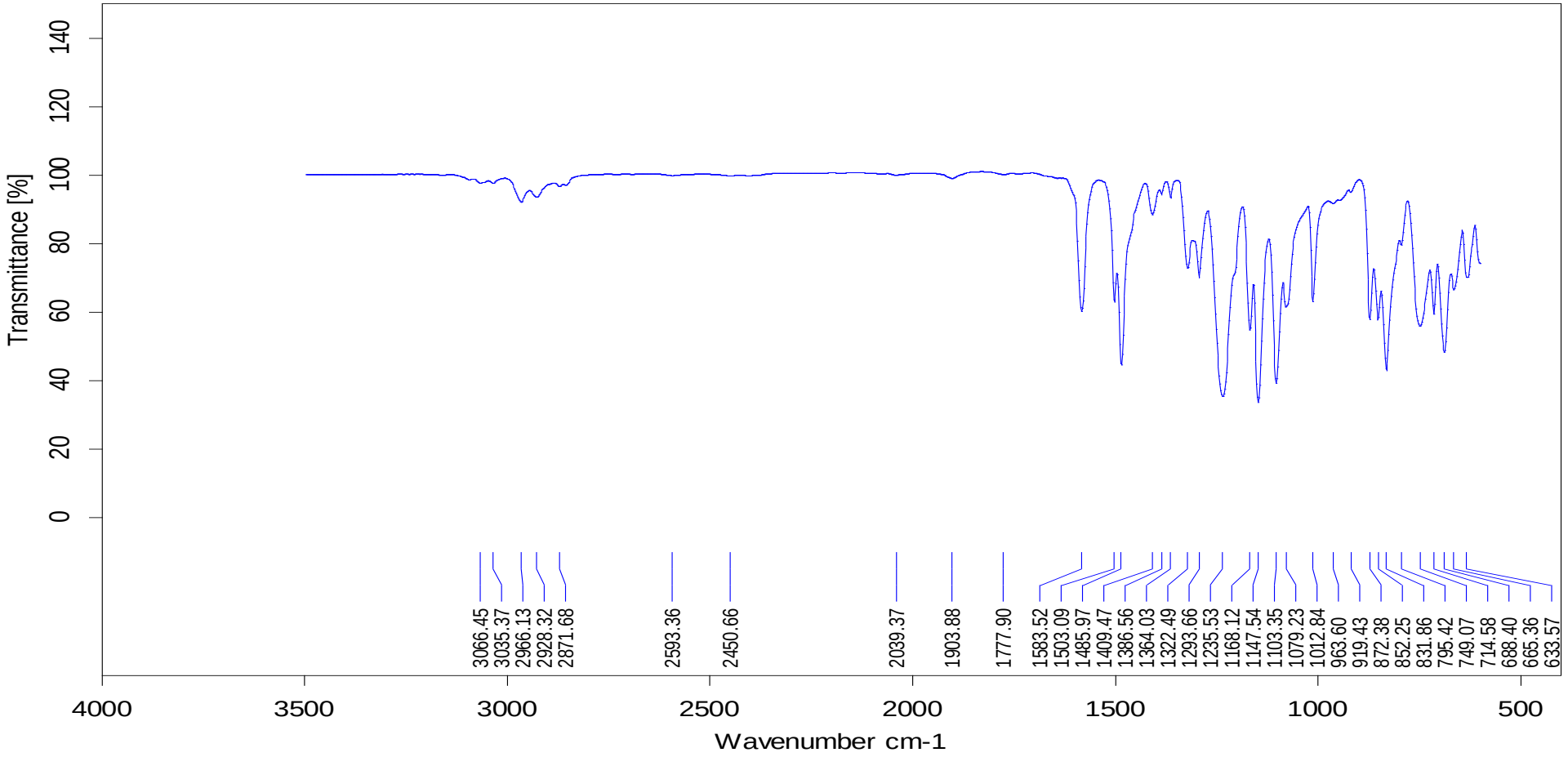
Appendix B

FTIR of carrier Aliquat 336



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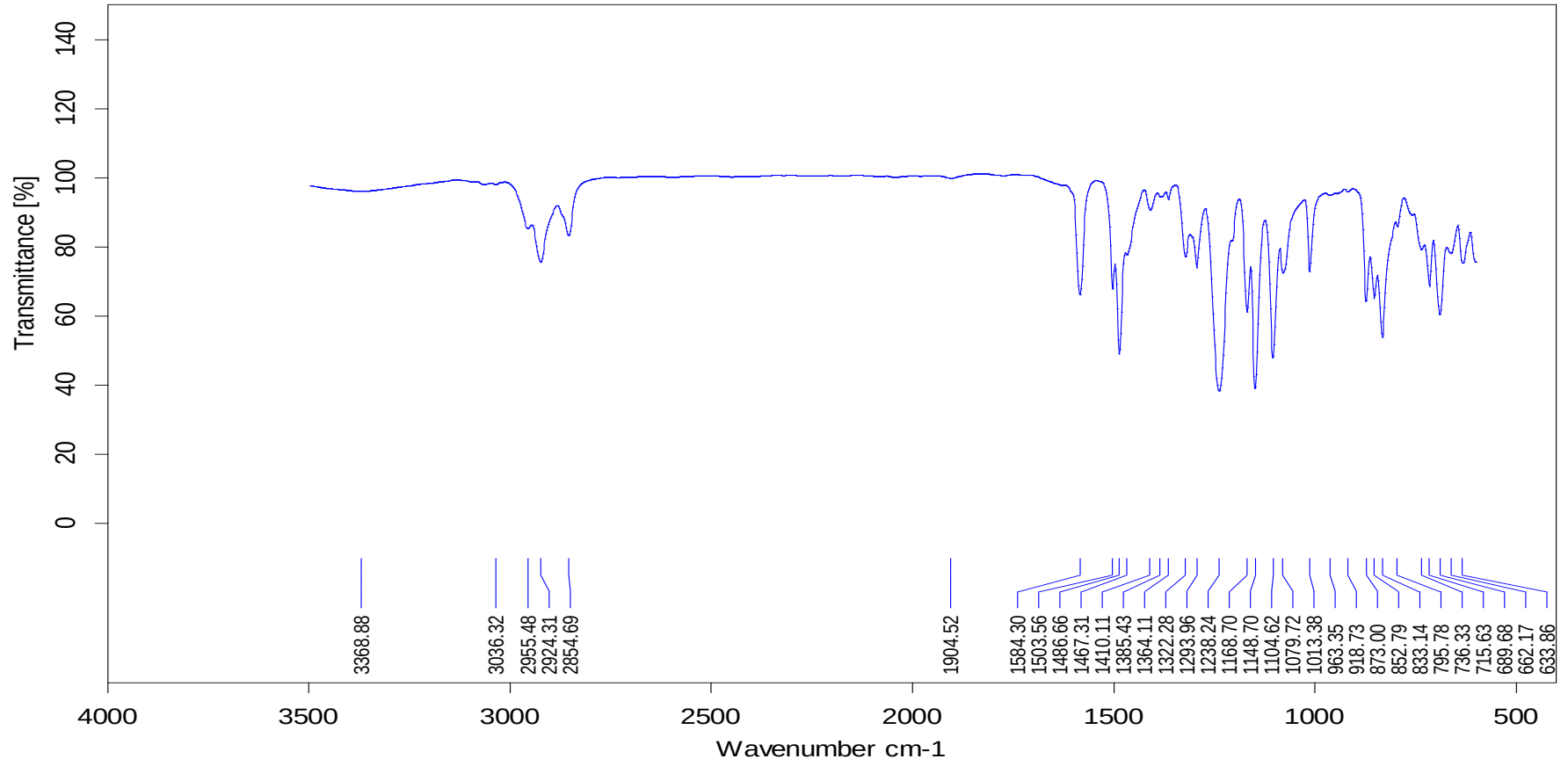
FTIR for Polysulfone



C:\Wits\AJvR\LMND\PhATUNH(CH2)2OH.3	Polymer	Solid	24/04/2018

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FTIR for the polysulfone based polymer inclusion membrane



C:\Wits\AJvR\LMND\PhATUNH(CH2)2OH.4	PIM	Solid		24/04/2018

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